

midpoint of the two P atoms for the two PPh₂ units. The smaller bond angles of *trans*-C—Mo—C for (I) [174.8 (3) vs 176.8 (2)^o] may be due to the rotational orientations of the phenyl groups of the bidentate ligands.

The authors would like to express their appreciation for the financial support of this work to the National Science Council (NSC79-0208-M003-04) and thank Dr Yu Wang (National Taiwan University, Taipei, Taiwan) for her kind help in using the diffractometer.

References

- BERNAL, I., REISNER, G. M., DOBSON, G. R. & DOBSON, C. B. (1986). *Inorg. Chim. Acta*, **121**, 199–206.
 CHEUNG, K. K., LAI, T. F. & MOK, K. S. (1971). *J. Chem. Soc. A*, pp. 1644–1647.
 CHOW, T. J., WANG, C.-Y., SHEU, S.-C. & PENG, S.-M. (1986). *J. Organomet. Chem.* **311**, 339–347.
 COTTON, F. A., DARENSBOURG, D. J., KLEIN, S. & KOLTHAMMER, B. W. S. (1982). *Inorg. Chem.* **21**, 294–299.
 COTTON, F. A. & KRAIHANZEL, C. S. (1962). *J. Am. Chem. Soc.* **84**, 4432–4444.
 Enraf-Nonius (1979). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
 GABE, E. J. & LEE, F. L. (1981). *Acta Cryst.* **A37**, S339.

Acta Cryst. (1991). **C47**, 525–528

Structures of (2-Cyanoethyl)(3-cyanopyridine)bis[dimethylglyoximato(1-)]cobalt(III) Monohydrate (I) and (4-Aminopyridine)(2-cyanoethyl)-bis[dimethylglyoximato(1-)]cobalt(III) (II)

BY AKIKO SEKINE AND YUJI OHASHI

Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

AND KAYAKO HORI

Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112, Japan

(Received 13 June 1990; accepted 14 August 1990)

Abstract. (I): [Co(C₃H₄N)(C₄H₇N₂O₂)₂(C₆H₄N₂)]·H₂O, *M_r* = 465.35, monoclinic, *P*₂₁/*n*, *a* = 18.425 (4), *b* = 12.073 (3), *c* = 10.038 (2) Å, β = 101.95 (2)^o, *V* = 2184.1 (4) Å³, *Z* = 4, *D_x* = 1.415 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 7.72 cm⁻¹, *F*(000) = 968, *R* = 0.061 for 3244 independent reflections. (II): [Co(C₃H₄N)(C₄H₇N₂O₂)₂(C₅H₆N₂)], *M_r* = 437.34, triclinic, *P* $\bar{1}$, *a* = 15.347 (5), *b* = 15.673 (7), *c* = 8.890 (3) Å, α = 104.46 (3), β = 105.74 (3), γ = 82.38 (5)^o, *V* = 1988 (1) Å³, *Z* = 4, *D_x* = 1.462 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 8.42 cm⁻¹, *F*(000) = 912, *R* = 0.080 for 6448 independent reflections. In each crystal, the 2-cyanoethyl group takes a conformation perpendicular to the cobaloxime plane. The size of the cavity for the 2-cyanoethyl group in crystal (II) is significantly greater than that in crystal (I). This explains the greater isomerization rate of (II) compared with (I) on exposure to visible light.

Introduction. It has been found that the 2-cyanoethyl group bonded to a Co atom in some cobaloxime complex crystals isomerizes to the 1-cyanoethyl

group 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 complexes with 3-ethylpyridine and 4-ethylpyridine as axial base ligands have the same conformation and that the rate of isomerization is closely related to the size of the cavity for the 2-cyanoethyl group in the two crystals (Sekine, Ohashi, Shimizu & Hori, 1991). Similar relation between the reaction rate and the cavity for the reactive group has been found for the crystalline-state racemization on exposure to X-rays (Ohashi, 1988). In order to examine whether the above relation holds good for the crystals with the other axial base ligands, two complexes with 3-cyanopyridine and 4-aminopyridine as axial ligands were prepared. The analyzed structures revealed that the conformations of the reactive 2-cyanoethyl groups are different from those of the 3-ethylpyridine and 4-ethylpyridine complexes. This paper reports the crystal structures of the two complexes and the relationship between the reaction cavity and the isomerization rate.

Experimental. (I) and (II) prepared in a way similar to that reported previously (Ohgo, Takeuchi, Natori, Yoshimura, Ohashi & Sasada, 1981); orange crystals recrystallized from aqueous methanol solution (I) and hot methanol solution with poor crystallinity (II). Crystal approximate dimensions 0.2 × 0.3 × 0.1 mm (I) and 0.3 × 0.3 × 0.1 mm (II). Rigaku AFC-4 (I) and AFC5R (II) diffractometer with graphite-crystal-monochromatized Mo K α radiation. Systematic absences: $0k0$ $k = 2n + 1$, $h0l$ $h + l = 2n + 1$ (I) and no absence (II). Cell parameters refined by least-squares method on basis of 20 (I) and 16 (II) independent 2θ values $20 < 2\theta < 30^\circ$. Three-dimensional intensity data collected up to $2\theta = 50^\circ$; range of hkl , -21 to 20 , 0 to 14 and 0 to 11 (I) and -18 to 17 , -18 to 18 and 0 to 10 (II). ω - 2θ scan technique, scan speed 4° min^{-1} (2θ) (I), 8° min^{-1} (2θ) (II). Three standard reflections showed no significant change in intensity. 3847 (I) and 7028 (II) intensities measured, 3244 (I) and 6448 (II) intensities with $|F_o| > 3\sigma(F_o)$ considered observed and used for the structure determination. Lorentz and polarization corrections, no absorption corrections ($\mu r \sim 0.25$). Structure solved by direct methods using MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refined by full-matrix least squares with SHELX76 (Sheldrick, 1976). One solvent water molecule appeared in a disordered position on a difference map in (I), all parameters including the occupancy factors refined.

H atoms located on a difference map except for those of disordered water molecules. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + C(F_o)^2]^{-1}$, $C = 0.0020$ (I) and 0.0040 (II). Final $R = 0.061$ (I) and 0.080 (II), $wR = 0.062$ (I) and 0.086 (II). In the final least-squares cycle, $(\Delta\sigma)_{\text{max}} 0.3$ (I) and 0.3 (II). Excursions in the final difference map, $+0.4$ and -0.4 (I) and $+0.7$ and -0.6 (II) $e \text{ \AA}^{-3}$. 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 (I) and (II) with numbering of atoms are shown in Figs. 1(a) and 1(b), respectively. For (II), one of the two independent molecules, molecule A, is shown since molecule B is very similar. Selected bond distances and angles and tor-

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 (I) and (II)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B(\AA^2)
(I)				
Co	70571 (3)	70900 (4)	7033 (5)	3.5
N(1)	6535 (2)	6712 (3)	2076 (4)	4.1
N(2)	6608 (2)	8469 (3)	888 (4)	4.5
N(3)	7558 (2)	7457 (3)	-692 (3)	4.3
N(4)	7505 (2)	5714 (3)	528 (4)	3.9
O(1)	6574 (2)	5697 (3)	2642 (3)	5.0
O(2)	6712 (2)	9380 (3)	151 (4)	6.1
O(3)	7521 (2)	8479 (3)	-1238 (3)	5.8
O(4)	7434 (2)	4824 (2)	1331 (3)	4.9
C(1)	6106 (2)	7477 (4)	2404 (5)	4.7
C(2)	6151 (3)	8519 (4)	1687 (5)	4.7
C(3)	7896 (2)	6658 (4)	-1171 (4)	4.6
C(4)	7874 (2)	5622 (4)	-432 (4)	4.4
C(5)	5628 (4)	7314 (6)	3424 (6)	7.0
C(6)	5701 (4)	9529 (5)	1859 (8)	7.3
C(7)	8271 (4)	6786 (7)	-2358 (6)	7.6
C(8)	8232 (4)	4567 (5)	-761 (6)	6.5
N(5)	9301 (3)	7684 (4)	5014 (4)	7.0
C(9)	7977 (2)	7544 (4)	2037 (4)	4.0
C(10)	8023 (3)	7210 (4)	3511 (4)	4.5
C(11)	8740 (3)	7475 (4)	4365 (4)	4.9
N(6)	6144 (2)	6612 (3)	-746 (4)	4.2
C(12)	5852 (3)	5592 (4)	-759 (5)	5.4
C(13)	5249 (3)	5266 (5)	-1719 (7)	6.9
C(14)	4912 (3)	6000 (5)	-2720 (6)	6.2
C(15)	5211 (2)	7044 (4)	-2717 (4)	4.8
C(16)	5824 (2)	7325 (4)	-1721 (5)	4.6
C(17)	4901 (2)	7884 (5)	-3683 (5)	5.6
N(7)	4652 (3)	8551 (5)	-4443 (5)	7.7
O(W1)†	865 (1)	1003 (1)	-44 (1)	11.8 (3)
O(W2)†	837 (1)	945 (1)	-65 (1)	13.4 (3)
(II)				
Co(A)	90408 (4)	26071 (4)	30077 (7)	2.4
N(1A)	10116 (3)	3195 (2)	3928 (5)	2.9
N(2A)	8742 (3)	3527 (2)	1902 (4)	2.9
N(3A)	7972 (3)	1994 (2)	2034 (5)	3.1
N(4A)	9323 (3)	1685 (3)	4115 (5)	3.1
O(1A)	10798 (2)	2915 (2)	5016 (5)	4.2
O(2A)	7925 (2)	3617 (2)	854 (4)	3.7
O(3A)	7322 (3)	2226 (3)	828 (4)	2.1
O(4A)	10114 (2)	1624 (2)	5262 (5)	4.1
C(1A)	10163 (3)	3893 (3)	3435 (6)	3.1
C(2A)	9338 (3)	4111 (3)	2280 (5)	3.1
C(3A)	7905 (4)	1317 (3)	2576 (6)	3.5
C(4A)	8704 (4)	1148 (3)	3859 (6)	3.4
C(5A)	10976 (4)	4437 (4)	4022 (8)	4.6
C(6A)	9213 (5)	4926 (4)	1618 (7)	4.4
C(7A)	7111 (4)	769 (4)	1960 (9)	5.4
C(8A)	8773 (4)	442 (4)	4762 (9)	5.2
N(5A)	11065 (5)	439 (5)	-690 (11)	10.2
C(9A)	9603 (4)	1888 (4)	1244 (7)	4.2
C(10A)	10423 (6)	1294 (6)	1754 (9)	6.9
C(11A)	10784 (5)	818 (5)	355 (11)	7.4
N(6A)	8424 (2)	3330 (2)	4746 (4)	2.3
C(12A)	8747 (3)	3310 (3)	6295 (5)	2.8
C(13A)	8284 (3)	3688 (3)	7455 (5)	3.2
C(14A)	7439 (3)	4127 (3)	7040 (6)	3.0
C(15A)	7106 (3)	4163 (3)	5429 (6)	3.2
C(16A)	7612 (3)	3767 (3)	4359 (5)	2.8
N(7A)	6937 (4)	4483 (4)	8108 (7)	4.5
Co(B)	60092 (4)	74411 (4)	67854 (8)	3.0
N(1B)	6691 (3)	8219 (3)	6318 (5)	3.3
N(2B)	6242 (3)	6727 (3)	4862 (5)	3.3
N(3B)	5374 (3)	6635 (3)	7279 (5)	3.5
N(4B)	5788 (3)	8136 (3)	8721 (5)	3.6
O(1B)	6866 (3)	9022 (2)	7270 (5)	4.4
O(2B)	5937 (3)	5912 (2)	4209 (5)	4.3
O(3B)	5255 (3)	5815 (2)	6388 (5)	4.2
O(4B)	6063 (3)	8963 (3)	9383 (6)	5.1
C(1B)	6963 (3)	7952 (3)	5017 (7)	3.6
C(2B)	6711 (3)	7051 (4)	4153 (7)	3.8
C(3B)	5083 (3)	6904 (4)	8580 (7)	3.9
C(4B)	5314 (4)	7804 (4)	9409 (7)	4.3
C(5B)	7469 (4)	8500 (4)	4426 (9)	5.0
C(6B)	6975 (5)	6554 (5)	2657 (8)	5.4

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53498 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Coordinates of these atoms are multiplied by 10^3 , and occupancy factors for O(W1) and O(W2) are 0.6 and 0.4, respectively.

Table 1 (cont.)

	x	y	z	B(Å ²)
C(7B)	4616 (5)	6318 (5)	9155 (9)	5.8
C(8B)	5041 (5)	8278 (5)	10920 (8)	6.2
N(5B)	9292 (4)	6705 (4)	10502 (7)	6.6
C(9B)	7163 (4)	6890 (4)	8003 (7)	4.2
C(10B)	7800 (7)	7467 (6)	9175 (16)	12.9
C(11B)	8640 (4)	7038 (4)	9937 (8)	4.9
N(6B)	4844 (3)	7999 (2)	5489 (5)	3.1
C(12B)	4240 (4)	7521 (3)	4343 (7)	3.7
C(13B)	3542 (4)	7852 (4)	3284 (7)	3.9
C(14B)	3412 (3)	8768 (3)	3409 (6)	3.0
C(15B)	4027 (3)	9279 (3)	4667 (6)	3.5
C(16B)	4702 (3)	8875 (3)	5636 (7)	3.8
N(7B)	2736 (4)	9145 (4)	2387 (7)	4.4

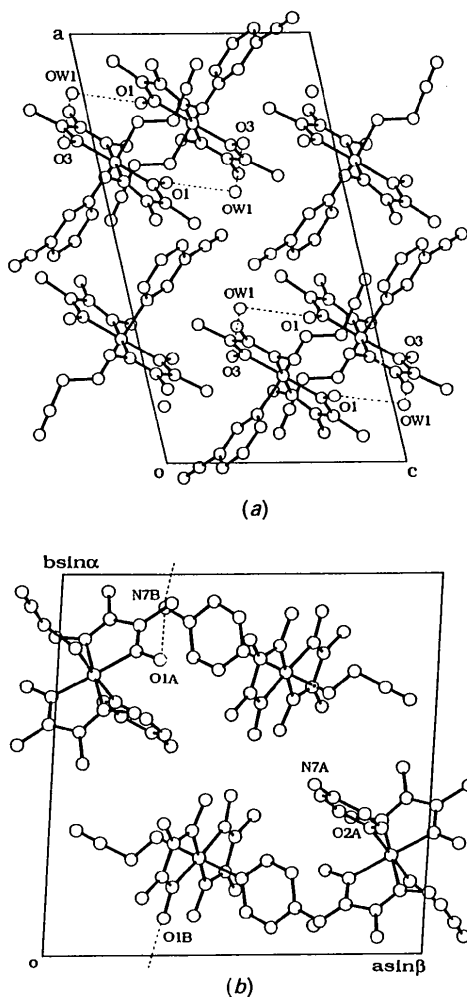
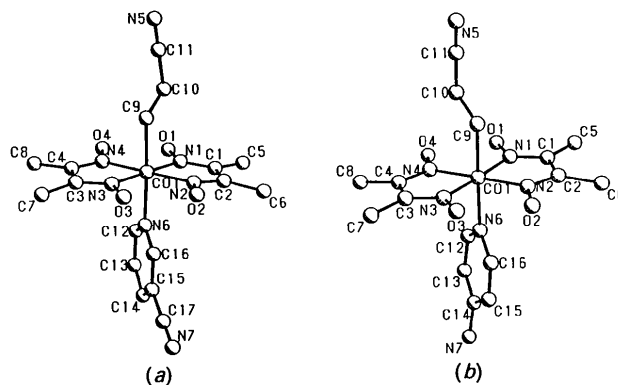


Fig. 1. Molecular structures of (a) (I), and (b) molecule A of (II), with the numbering of the atoms.

sion angles are listed in Table 2. The Co—C distances, 2.006 (5) Å for (I) and 2.017 (6) Å for A and 2.019 (7) Å for B of (II) and the Co—N(6) distances, 2.066 (4) for (I) and 2.050 (4) Å for molecule A and 2.064 (4) Å for molecule B of (II) are approximately the same as in related pyridine complexes: two forms of 3-methylpyridine complex (Uchida, Danno,

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

	(I)	(II)	
		A	B
Co(1)—N(1)	1.892 (4)	1.880 (4)	1.893 (5)
Co(1)—N(2)	1.886 (4)	1.882 (4)	1.890 (4)
Co(1)—N(3)	1.883 (4)	1.897 (4)	1.890 (5)
Co(1)—N(4)	1.879 (4)	1.886 (4)	1.883 (5)
Co(1)—C(9)	2.006 (5)	2.017 (6)	2.019 (7)
Co(1)—N(6)	2.066 (4)	2.050 (4)	2.064 (4)
N(1)—Co(1)—N(2)	80.9 (2)	81.9 (2)	81.1 (2)
N(1)—Co(1)—N(3)	178.7 (2)	178.4 (2)	177.6 (2)
N(1)—Co(1)—N(4)	98.9 (2)	98.8 (2)	99.4 (2)
N(1)—Co(1)—C(9)	93.8 (2)	89.0 (2)	90.1 (2)
N(1)—Co(1)—N(6)	89.0 (2)	92.9 (2)	88.9 (2)
N(2)—Co(1)—N(3)	99.1 (2)	98.2 (2)	98.2 (2)
N(2)—Co(1)—N(4)	179.7 (2)	179.2 (2)	179.0 (2)
N(2)—Co(1)—C(9)	91.2 (2)	88.9 (2)	88.6 (2)
N(2)—Co(1)—N(6)	90.3 (2)	90.6 (2)	90.1 (2)
N(3)—Co(1)—N(4)	81.1 (2)	81.2 (2)	81.2 (2)
N(3)—Co(1)—C(9)	87.5 (2)	89.3 (2)	87.5 (2)
N(3)—Co(1)—N(6)	89.7 (2)	88.8 (2)	93.4 (2)
N(4)—Co(1)—C(9)	88.7 (2)	91.6 (2)	90.5 (2)
N(4)—Co(1)—N(6)	89.8 (1)	88.9 (2)	90.8 (2)
C(9)—Co(1)—N(6)	177.0 (2)	177.9 (2)	178.5 (2)
N(1)—Co(1)—N(6)—C(12)	56.5 (4)	61.8 (6)	-128.8 (8)
N(1)—Co(1)—C(9)—C(10)	-13.3 (4)	-63.7 (7)	-49.2 (4)
Co(1)—C(9)—C(10)—C(11)	-174.1 (4)	178.6 (6)	176.3 (6)

Fig. 2. Crystal structures (a) viewed along the *b* axis for (I) and (b) viewed along the *c* axis for (II). The lower-occupancy water O atom, O(W2), of (I) is omitted for clarity.

Sasada & Ohashi, 1987) and 3-ethylpyridine and 4-ethylpyridine complexes (Sekine, Ohashi, Shimizu & Hori, 1991). The Co—C distance range is 1.997 (9)–2.027 (7) Å and the Co—N(5) distances are 2.056 (4)–2.076 (5) Å. The Co—N(equatorial) distances are in the range 1.871 (3)–1.896 (6) Å, and are nearly equal to the corresponding ones in the cobaloxime complexes determined so far. The torsion angles Co—C(9)—C(10)—C(11) are -174.1 (4) (I) and 178.6 (6) (A) and 176.3 (6)° (B) (II). This causes the 2-cyanoethyl groups of (I) and (II) to take a conformation perpendicular to the cobaloxime plane. Such a perpendicular conformation was also found in form II of a pyridine complex (Uchida, 1985).

The crystal structures of (I) and (II) are shown in Figs. 2(a) and 2(b), respectively. The crystal of (I) contains one water molecule per asymmetric unit, although it occupies two disordered positions,

O(W1) and O(W2). Both O(W1) and O(W2) are hydrogen bonded to O(1) and O(3) of the neighboring molecules, so the cobaloxime complexes are connected along the *b* axis. In (II), one of the H atoms of the amino group of *A* is hydrogen bonded to the O(2*A*) atom of a neighboring molecule, and the two H atoms of the amino group of *B* are hydrogen bonded to O(1*A*) and O(1*B*) atoms of neighboring molecules. Except for this hydrogen bonding there are no short contacts between the molecules in both crystals.

The reaction cavities for the 2-cyanoethyl groups of (I) and (II) were drawn (Ohashi, Uchida, Sasada & Ohgo, 1983) and the volumes of the cavities were calculated to be 12.24 Å³ for (I) and 13.31 Å³ for *A* and 16.69 Å³ for *B* of (II), respectively. The average value for (II) is 14.99 Å³. The rates of isomerization were obtained from the change of IR spectra of the C≡N stretching mode, assuming first-order kinetics in the early stages (Sekine, 1989). The rate constants for (I) and (II) are 1.2×10^{-4} and $1.5 \times 10^{-4} \text{ s}^{-1}$, respectively. The relation between the reaction cavity and the isomerization rate holds good for the present crystals, as observed in the crystals of 3-ethylpyridine and 4-ethylpyridine complexes (Sekine, Ohashi, Shimizu & Hori, 1991), although the conformations of 2-cyanoethyl groups in 3-ethylpyridine and 4-ethylpyridine complexes are parallel to the cobaloxime plane, whereas those in (I) and (III) take perpendicular conformations. This may indicate that

the β - α (2→1) photoisomerization is controlled by the crystalline lattice in the early stages in spite of the different conformation of the reactive group.

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan. We thank Professor Y. Ohgo and Dr S. Baba for their valuable discussion, and Miss E. Shimizu for assistance with the crystal structure determination.

References

- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- OHASHI, Y. (1988). *Acc. Chem. Res.* **21**, 268–274.
- OHASHI, Y., UCHIDA, A., SASADA, Y. & OHGO, Y. (1983). *Acta Cryst.* **B39**, 54–61.
- OHGO, Y. & TAKEUCHI, S. (1985). *J. Chem. Soc. Chem. Commun.* pp. 21–23.
- OHGO, Y., TAKEUCHI, S., NATORI, Y., YOSHIMURA, J., OHASHI, Y. & SASADA, Y. (1981). *Bull. Chem. Soc. Jpn.* **54**, 3095–3099.
- SEKINE, A. (1989). Masters thesis, Ochanomizu Univ., Japan.
- SEKINE, A., OHASHI, Y., SHIMIZU, E. & HORI, K. (1991). *Acta Cryst.* **C47**, 53–56.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- UCHIDA, A. (1985). Doctorate thesis, Tokyo Institute of Technology, Japan.
- UCHIDA, A., DANNNO, M., SASADA, Y. & OHASHI, Y. (1987). *Acta Cryst.* **B43**, 528–532.

Acta Cryst. (1991). **C47**, 528–531

Structure of Zinc(II) (*RS*)-1-Isopropyl Citrate Tetrahydrate

BY SUMIKO TSUJI, TADASHI SHIBATA AND YOSHIO ITO

Osaka Branch, National Institute of Hygienic Sciences, 1-1-43 Hoenzaka, Chuo-ku, Osaka 540, Japan

AND SATOSHI FUJII AND KEN-ICHI TOMITA

Faculty of Pharmaceutical Sciences, Osaka University, 1-6 Yamadaoka, Suita, Osaka 565, Japan

(Received 7 June 1990; accepted 14 August 1990)

Abstract. *catena*-Poly{diaquazinc- μ -[1-isopropyl citrato(2-)- κ O, κ O', κ O'': κ O''']}, [Zn(C₉H₁₂O₇)(H₂O)₂].2H₂O, *M*_r = 369.62, monoclinic, *P*2₁/*c*, *a* = 9.934 (4), *b* = 29.692 (3), *c* = 8.941 (4) Å, β = 144.73 (2)°, *V* = 1522.7 (7) Å³, *Z* = 4, *D*_m = 1.610 (3), *D*_x = 1.612 Mg m⁻³, λ (Cu *K* α) = 1.54178 Å, μ = 2.741 mm⁻¹, *F*(000) = 768, *T* = 283 K, final *R* = 0.0346 for 2089 observed reflections. Each 1-isopropyl citrate chelates to a diaquazinc ion in a tridentate manner through the end carboxyl, the

central carboxyl and the hydroxyl O atoms and bridges another diaquazinc ion with its end carboxyl O atom. This leads to extended chelated strips with bridged Zn atoms. Other water molecules are hydrogen bonded to the aqua ligands or 1-isopropyl citrates of the chelated strips. The strips are packed through van der Waals bonds.

Introduction. Isopropyl citrate, which is more oil soluble than citric acid, has been developed as a