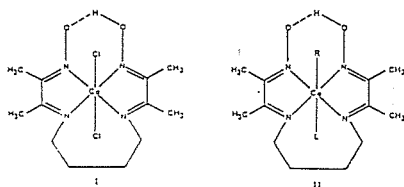


09.4-15 ORGANOCOBALT COMPLEXES WITH A BUCKLED EQUATORIAL LIGAND. By V. B. Pett, R. W. Jones, A. M. Mulichak, P. L. Choo, J. W. Bacon, D. E. Zacharias, J. P. Glusker, Department of Chemistry, The College of Wooster, Wooster, Ohio 44691.

New cobalt complexes I and II have been synthesized, where R = methyl, ethyl, 2-methylpropyl, and L = OH₂, imidazole. These complexes, in which the equatorial ligand is distorted due to a seven-membered chelate ring, may serve as models for B₁₂ coenzyme, since the equatorial corrin ring in that compound is ruffled.

Synthesis of the equatorial ligand was adapted from literature reports (Martin, J.W.L. et al. *Inorg. Chem.* (1981) 20, 814). I is prepared by mixing the equatorial ligand with CoCl₂ in acetone under argon, followed by exposure to air. II is obtained as the ClO₄ salt by alkylation of I with RI in the presence of NaBH₄ and water or imidazole, followed by recrystallization from HClO₄. Elemental analyses, as well as ¹H and ¹³C NMR spectra are consistent with the structures shown.



I crystallizes in space group P2₁2₁2₁, a = 14.017(2), b = 29.014(4), c = 8.005(2) Å, Z = 8. Anisotropic refinement of 2915 data gave R = 0.06, R_w = 0.08. The "fold angle" between the two halves of the ligand is 4° and 12° in the two molecules, which is as much as that observed in other complexes with considerably more steric demand from axial ligands (Parker, W.O., Jr. et al. *Inorg. Chem.* (1985) 24, 3908).

Likewise, the first structure of an organocobalt complex II (R = ethyl, L = OH₂) in this series shows that the equatorial ligand is appreciably buckled (fold angle -7°). [C2/c, a = 21.566(5), b = 7.330(3), c = 25.172(6) Å, β = 100.97(2), Z = 8, 2229 data; relatively high residuals, R = 0.10, R_w = 0.13, were due to disordered ClO₄.] The Co-C bond length is somewhat longer (2.010(8) Å) than similar dimethylglyoxime and "Costa" B₁₂ models (Marzilli, L. G. et al. *Inorg. Chim. Acta* (1985) 107, 139), probably due to the additional steric demand of the equatorial ligand.



09.4-16 CRYSTAL STRUCTURES OF SOME COMPLEXES OF LANTHANIDES AND AMINO ACIDS. By Zheng Yifan, and Pan Kazhen. Fujian Institute of Research on the Structure of Matter, Academia Sinica, Fuzhou, China.

Some complexes were prepared from an aqueous solution or 50% dioxane solution containing praseodymium perchlorate and α-amino acids. Intensity data have been collected on a CAD-4 diffractometer.

There are two types of crystal structure (Type 1 and Type 2). In type 1, a pair of adjacent metal ions are bridged by four carboxylate groups, while the type 2 has an infinite three-dimensional network with carboxyl bridging group. In these two types of structure, the amino group in amino acids is not coordinated to Ln³⁺, and the carboxyl groups in amino acids are dissociated and act as the bidentate bridging ligands, of which two oxygen atoms are coordinated to different metal ions. The metal ions are separated from each other by a distance of more than 4 Å, so that there are no metal-metal bond between them. There are two types of structure in Glycine, but only first structure type in Methionine. For different Ln³⁺ ion, however, there are different structures in Serine. They suggest that steric effect play a predominant role in determining structures of the complexes of Ln³⁺ and amino acids.

Table of the crystallographic data.

complex	space group	a(Å) α	b(Å) β	c(Å) γ	Z	R	Type of structure
Er(ClO ₄) ₃ (Dio) ₃ ·10H ₂ O	P2 ₁ /n	11.229	24.836	12.951	4	0.079	
Er(Gly) ₂ (Dio) ₄ (ClO ₄) ₃ ·6H ₂ O	P1	11.475	11.165	14.092	4	0.055	1
Er ₂ (Ser) ₃ (Dio) ₄ (ClO ₄) ₆ ·10H ₂ O	C2	15.975	15.974	15.280	4	0.059	1
Er ₂ (Gly) ₃ (Met) ₃ (ClO ₄) ₆ ·12H ₂ O	P1	12.375	14.041	19.074	4	0.091	1
Eu ₂ (Gly) ₃ (Met) ₃ (ClO ₄) ₆ ·12H ₂ O	P2 ₁ /n	13.897	21.770	19.127	8	0.074	1
Pr(Gly) ₃ (ClO ₄) ₃ ·7H ₂ O*	P1	11.558	14.126	15.677	4	0.043	2
Pr(Ser) ₃ (ClO ₄) ₃ ·2H ₂ O*	P1	9.339	12.881	13.215	2	0.062	2
Er(Gly) ₃ (ClO ₄) ₃ ·7H ₂ O	P1	11.476	14.028	15.443			2
Eu ₂ (Ser) ₃ (Dio) ₄ (ClO ₄) ₆ ·10H ₂ O	C2	16.082	16.067	15.374			1

* Li Xuyue and Pan Kazhen, *J. of structural chemistry* (1985) 4, 56.

