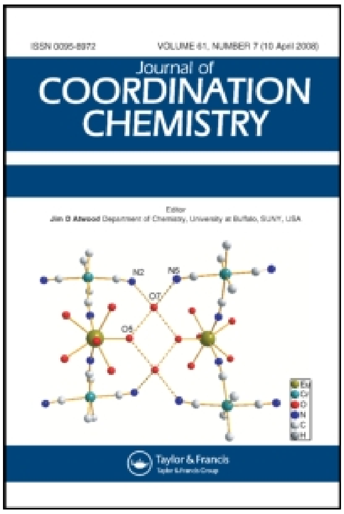

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SHORT COMMUNICATION

Strain Energy Minimization and Conformational Analysis of Mixed Ligand Complexes of Cobalt(III) with the Flexible Tetramine Ligand N,N -Bis-(2-picolyl)-1,2(S)-propanediamine and some Amino Acids

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We have recently reported the results of a conformational analysis (strain energy minimization calculation) of the stereoisomers of some cobalt (III) complexes with the stereospecific chelating agent N,N′-bis-(2-picolyl)-1,2(S)-propanediamine (picpn)[1]. We have extended these calculations to include the mixed ligand complexes, $[Co(picpn)gly]^{2+}$, $[Co(picpn)R\text{-}ala]^{2+}$ and $[Co(picpn)S\text{-}ala]^{2+}$. Our interest in these compounds arises from recent reports of the synthesis of optically active amino acids *via* hydrogenation of appropriate precursors in the presence of chiral metal complexes[2,3,4], one of which contains heterocyclic nitrogen donors.[5]

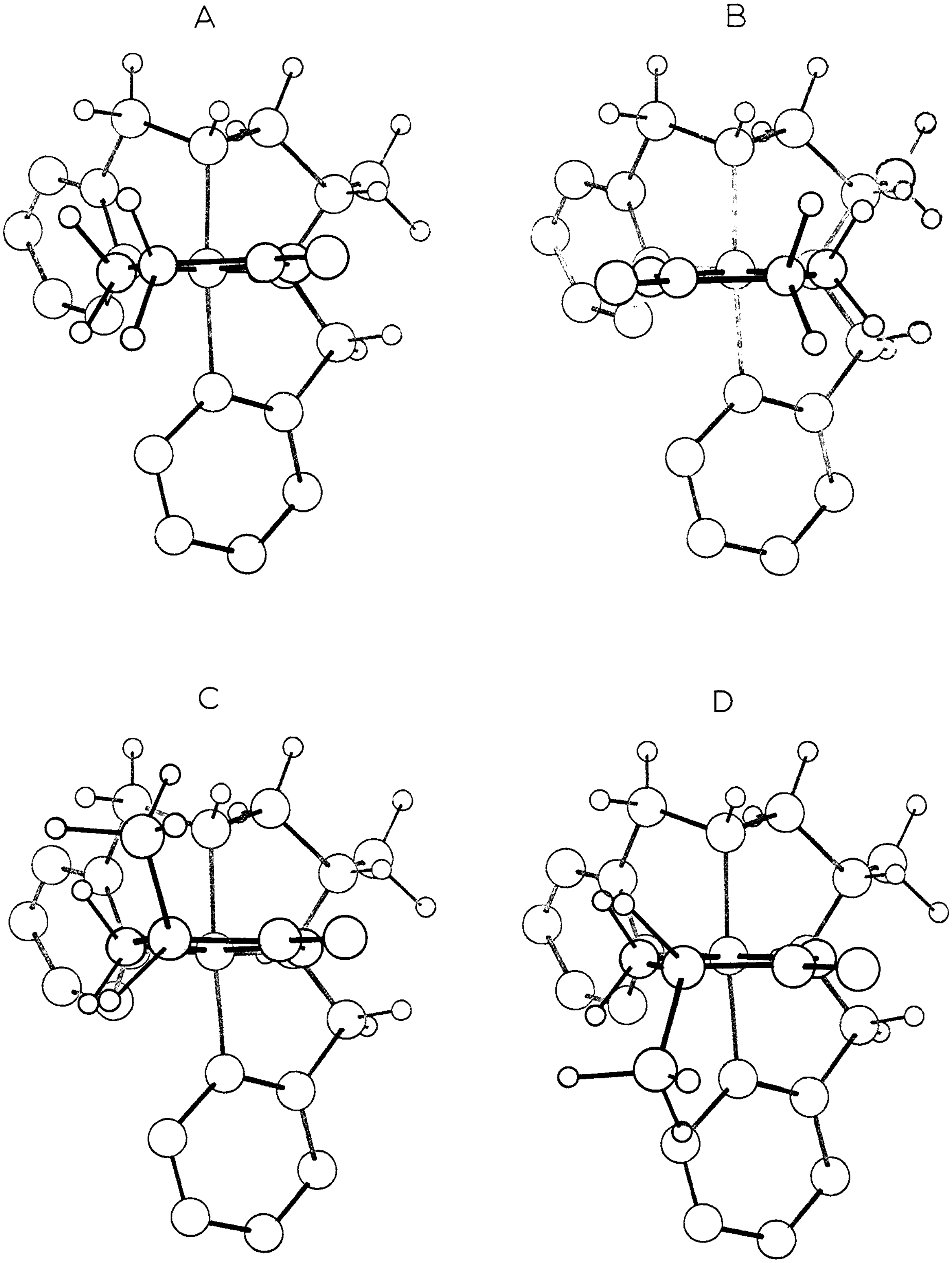
The calculations were performed by standard methods which have been described in detail elsewhere[1]. A preliminary coordinate set for the glycine derivatives was obtained from the corresponding oxalato complex, and the strain energy minimization routine was initiated with minor changes in the atom designations and interaction parameters. After a few cycles, the program had effectively converted the oxalato dianion into the glycinato ligand. The alanine complex was similarly "prepared" from the appropriate glycine derivative. Convergence (rms coordinate shift $\leqslant 0.08$ A) was reached in 15 cycles or less for each of the complexes under consideration. The final energy terms are given in Table 1, and the structures of the complexes are shown in Figure 1.

For either the uns_1 or uns_2 topology, we find the R-alanine complex about 0.6–0.7 kcal/mole lower in energy than the S-alanine derivative; the difference between uns_1 and uns_2 isomers for a given amino acid is of comparable magnitude. We find the minimized energy difference between the glycine and alanine complexes rather interesting. Note that the difference between the uns_1 and uns_2 isomer is about the same for all three series, but that the minimized energy for the glycine complexes lies *between* that of the alanine derivatives. We attribute this difference to a lowering of the repulsion terms derived from non-bonded interactions with the α-methylene group of glycine when one proton is replaced by a methyl group. In our model, the methyl group is free to rotate to a position of minimum energy which effectively *increases* the CH_3-picpn distance for the R-alanine isomers over the α-methylene-picpn dis-

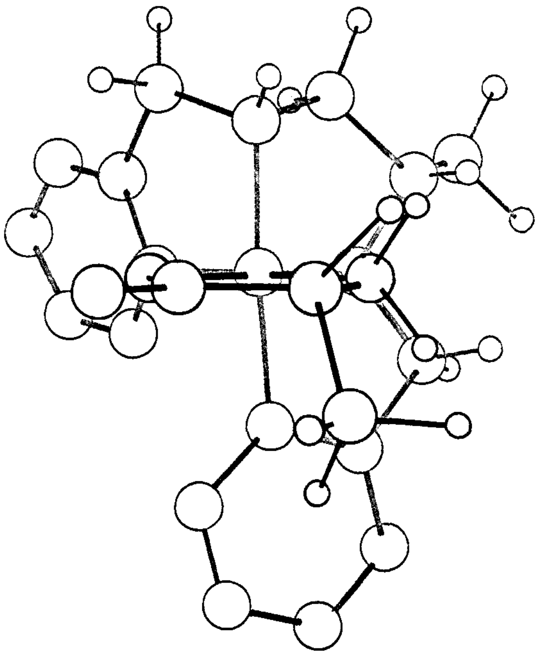
TABLE I. Final energy terms (kcal/mole) from minimization

	O	A	B	C	D	E	F
Bond Deformation	0.23	0.46	0.49	0.42	0.48	0.45	0.63
Non Bonded Interactions		1.86	3.33	2.83	3.97	2.58	2.67
		1.57	2.59	2.55	2.80	2.38	2.23
	0.64	0.29	0.74	0.28	1.17	0.20	0.44
Valence Angle Distortion	6.12	7.03	6.94	7.45	7.37	6.38	6.33
Torsion	2.24	2.44	2.83	2.70	2.60	2.93	3.07
Total	9.24	10.34	11.03	10.86	11.63	10.00	10.64

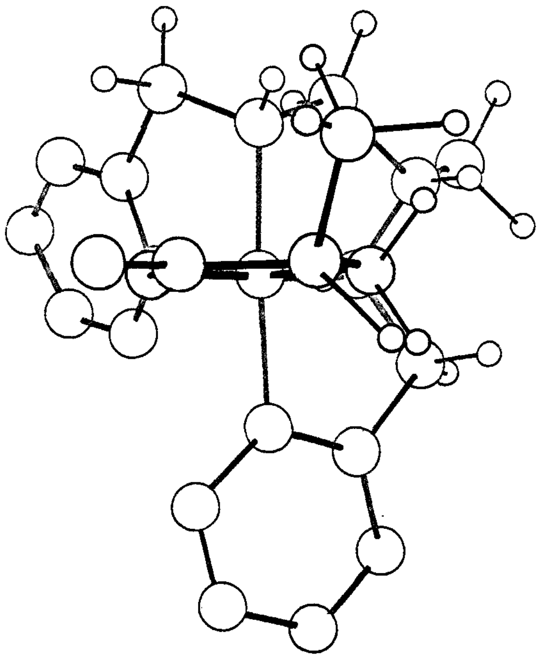
O = Δ-uns-*cis*-[Co picpn X_2] (G. R. Brubaker and R. A. Euler, *Inorg. Chem.* **11**, 2357 (1972).
A = Δ-uns_2-[Co picpn gly]
B = Δ-uns_1-[Co picpn gly]
C = Δ-uns_2-[Co picpn R ala]
D = Δ-uns_2-[Co picpn S ala]
E = Δ-uns_1-[Co picpn R ala]
F = Δ-uns_1-[Co picpn S ala]


A
B
C
D

E



F



tance in the glycine isomers. The corresponding distances are, of course, decreased and the non-bonded repulsion terms increased, for the S-alanine isomers. The energy differences we calculate are comparable with those estimated for cobalt(III) complexes which produce isomer distributions comparable with those obtained with chiral catalysts (i.e., an energy difference between isomers of 0.3 4.0 kcal/mole corresponds to 60–80% optical purity)[6].

The tetramine ligand, picpn, is shown in the configuration which has been observed experimentally[7], and which has been shown to lie lowest in conformational energy using our interaction set[1]. It is most likely the configuration adopted by this ligand when coordinated about any six coordinate metal ion. The energy differences among the stereoisomers of the mixed ligand amino acid complexes are comparable to the energy differences to be expected among the products of a catalytic hydrogenation which proceeds to a chelated product, or, more reasonably, to the energy differences among the labile intermediates in a process which proceeds through chelate ring formation.

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