

# Investigation of Geometrical and Conformational Isomers of Cobalt(II) Bis(diphenylacetato)-bis( $\gamma$ -picolinate) by Dynamic NMR Spectroscopy and Molecular Mechanics

G. V. Novitskii<sup>1</sup>, Al. Chekal<sup>2</sup>, and A. P. Gulya<sup>1</sup>

<sup>1</sup>Moldova State University, ul. Matteevicha 60, Chisinau, 277009 Moldova

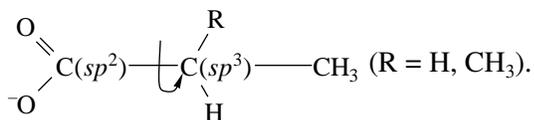
<sup>2</sup>Al. I. Cuza University, Jassy, Romania

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**Abstract**—Cobalt(II) bis(diphenylacetato)-bis( $\gamma$ -picolinate) is synthesized and its geometrical and conformational isomers are investigated using dynamic NMR and molecular mechanics methods. The complex in the solution is shown to exist as *cis* and *trans* isomers, which are detected at 263 K in the course of a slow intermolecular ligand exchange. At  $T < 223$  K, the intramolecular rotation of the phenyl radicals about the  $^-O_2C-CH(Ph)_2$  and  $^-O_2CCH(Ph)-Ph$  bonds slows, which results in the formation of different conformers. The energies of the retarded intermolecular exchange and of the retarded rotation of the phenyl radicals were calculated from  $^1H$  NMR and molecular mechanics data.

Dynamic NMR spectroscopy is successfully employed in stereochemical studies of labile cobalt(II) complexes in solutions. It was established [1–4] that in isotropic paramagnetic shifts of cobalt(II) coordination compounds, the predominating pseudocontact (dipole) component is specified by the coordinates of the resonant nucleus and the  $g$  factor of the complex.

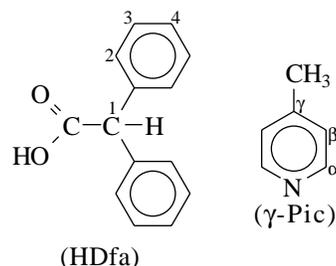
It is worth noting that the NMR spectroscopic method can be used for studying paramagnetic complexes, especially geometrical and conformational isomers [5], provided that the spin-electron relaxation in these systems varies within  $10^{-9}$ – $10^{-11}$  s [6]. Earlier [7], we investigated the geometrical and conformational isomerism of adducts of cobalt(II) mono- and dimethylacetate with  $\gamma$ -picoline by dynamic NMR spectroscopy. It was established that the signals registered under slow (in terms of the NMR time scale) intramolecular ligand exchange are due to the *cis*, *trans* isomers and to different conformers. The latter, however, appear only upon the retarded rotation about the  $C_{sp^2}-C_{sp^3}$  bond:



Analogous conformers were also detected for the *cis* isomers of adducts of Co(II) adamantanate [8] and Co(II) trifluoroacetate [9] with  $\gamma$ -picoline.

This work was undertaken to study the conformational transformations occurring in the Co(II) diphenylacetate complex with  $\gamma$ -picoline, in which the Dfa<sup>-</sup>

ligand produces significant steric hindrances.



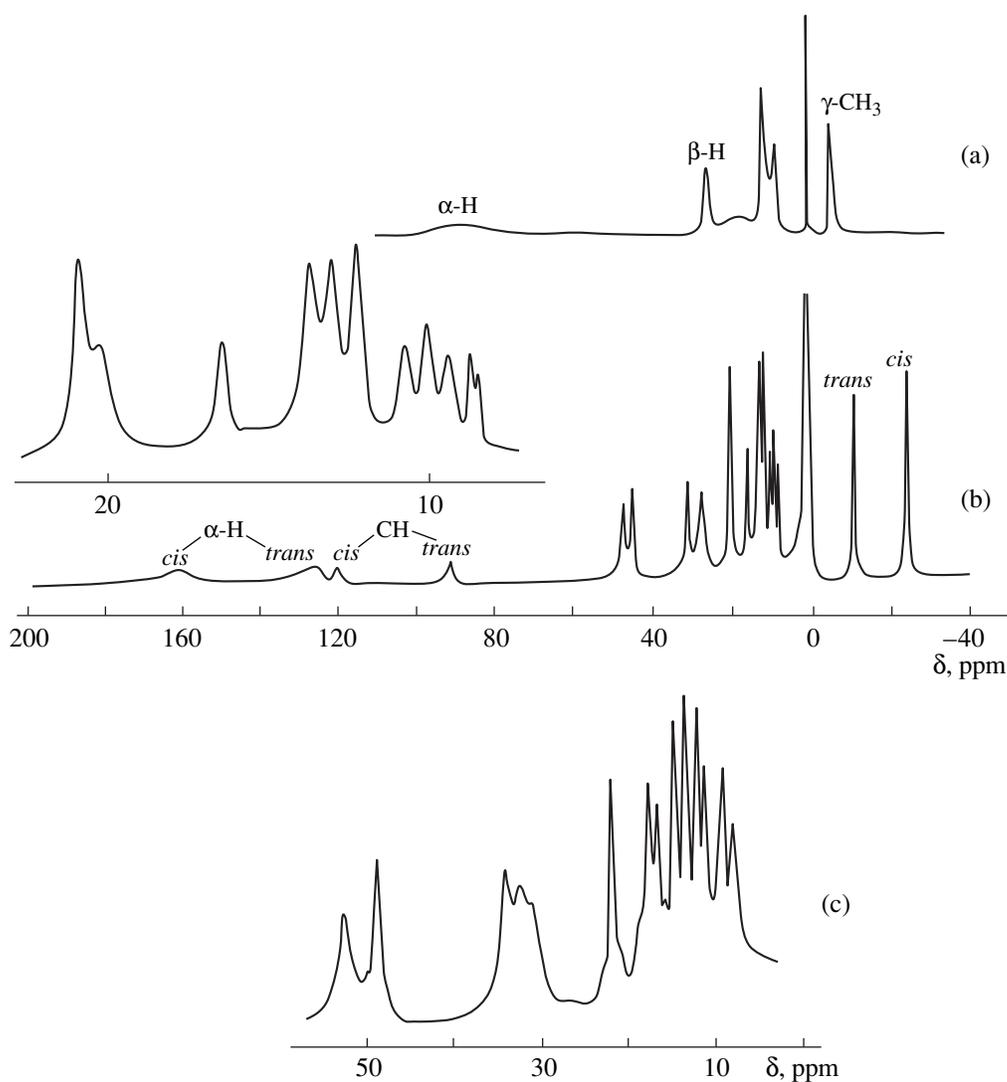
## EXPERIMENTAL

Magnetic measurements were carried out using the Gouy method;  $Hg[Co(CNS)_4]$  was used as the standard for calibration.

The IR absorption spectra were taken on a Specord M-80 spectrophotometer with the samples suspended in mineral oil.

The  $^1H$  NMR spectra of the complex dissolved in  $CDCl_3$  were recorded on a Bruker WP-80 instrument equipped with a device for low-temperature measurements. Tetramethylsilane was used as the internal standard.

**Synthesis of  $[Co(\gamma\text{-Pic})_2(\text{Dfa})_2]$  (I).** Cobalt(II) acetate (2.5 g, 0.01 mol) was dissolved in 70 ml of methanol. Sodium diphenylacetate (4.68 g, 0.02 mol) was then added with heating and stirring. The mixture was allowed to stand for 24 h; the precipitate was filtered off and dried at  $140^\circ C$ . The obtained lilac-colored substance was dissolved in chloroform containing  $\gamma$ -picoline. After the solvent was partially evaporated, the



**Fig. 1.**  $^1\text{H}$  NMR spectra of  $[\text{Co}(\gamma\text{-Pic})_2(\text{Dfa})_2]$  in  $\text{CDCl}_3$  at (a)  $T = 300$ , (b)  $T = 233$ , and (c)  $T = 213$  K.

title compound precipitated as pink crystals readily soluble in organic solvents.

According to elemental analysis data, the composition of the compound is  $[\text{Co}(\gamma\text{-Pic})_2(\text{Dfa})_2]$ .

For  $\text{CoC}_{40}\text{H}_{36}\text{N}_2\text{O}_4$

anal. calcd. (%): Co, 8.85; C, 71.96; H, 5.40; N, 4.20.

Found (%): Co, 8.80; C, 72.01; H, 5.44; N, 4.23.

## RESULTS AND DISCUSSION

The magnetic measurements of the obtained compound gave  $\mu_{\text{eff}} = 4.97 \mu_{\text{B}}$ , which suggests an octahedral environment and a high-spin state of cobalt(II) in structure **I** [10].

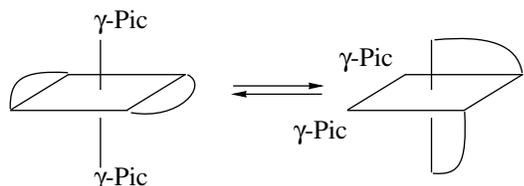
The IR spectrum of compound **I** contains bands of stretching vibrations  $\nu(\text{C}=\text{N}) = 1632$  and  $\nu(\text{C}=\text{C}) = 1520 \text{ cm}^{-1}$  of the coordinated  $\gamma$ -picoline. The positions

of bands of the stretching vibrations of the carboxyl group ( $\nu_{\text{as}}(\text{COO}) = 1601$  and  $\nu_{\text{s}}(\text{COO}) = 1403 \text{ cm}^{-1}$ ) are evidence of its bidentate coordination [11].

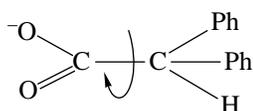
The  $^1\text{H}$  NMR spectrum taken at room temperature (Fig. 1a) shows six signals with chemical shifts of 90.0, 25.5, 20.4, 10.8, 9.4, and  $-5.4$  ppm and an intensity of ratio 2 : 2 : 1 : 8 : 2 : 3, indicating that the complex composition remains unchanged in a solution. The signals at 90.0, 25.5, and  $-5.4$  ppm are assigned to the protons of the respective  $\alpha$ -CH,  $\beta$ -CH, and  $\gamma$ -CH<sub>3</sub> groups of the coordinated  $\gamma$ -picoline [6–8]. The other signals correspond to the protons in positions 1, 2(2') + 3(3'), and 4 in the diphenylacetate moiety.

Three regions of intermolecular and intramolecular ligand exchange in solution **I** can be identified on the temperature dependence of the dynamic NMR parameters: 298–273 K (rapid exchange), 273–253 K (average exchange), and the region below 253 K (slow

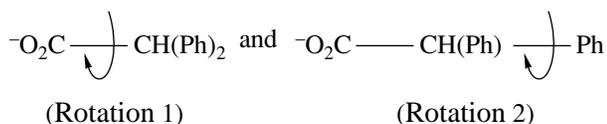
exchange) (Figs. 1a, 1b). In the slow exchange region, signals from  $\alpha$ -CH,  $\beta$ -CH, and  $\gamma$ -CH<sub>3</sub> groups split into two equal-intensity signals, which we assigned to *cis* and *trans* isomers [6–8].



The <sup>1</sup>H NMR spectrum of the diphenylacetate moiety at 233 K (Fig. 1b) exhibits 12 signals of different intensity. With a decrease in temperature to 213 K (Fig. 1c), the number of signals increased even more, while the number of lines corresponding to  $\gamma$ -picoline moiety remained the same. This fact may be explained, as in [7], by the presence of conformers due to magnetically inequivalent positions occupied by two phenyl radicals relative to the anisotropic dipole surfaces of a central atom during retarded rotation about the bond.



To establish the details of the conformational processes occurring as a result of the change in the geometry of the acido ligand, we estimated the energy of the retarded rotation around the bonds:



Calculations were carried out by the molecular mechanics technique using the MMC program with standard parametrization [12–14].

The data obtained show that the most stable conformations

Angle	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_4$	$\alpha_5$	$\beta_1$	$\beta_2$	$\beta_3$	$\beta_4$	$\beta_5$
$\alpha_i(\beta_i)$ , deg	44.93	109.87	24.87	112.73	67.60	93.93	86.63	47.02	120.16	12.82

The plots of the potential energy vs. the angle of internal rotation about the above-mentioned bonds are shown in Fig. 2. For rotation 2, the potential energy curve exhibits two maxima with nearly equal energy (26.37 and 29.17 kkal/mol) and two minima, while the curve for rotation 1 contains three maxima and three minima (Fig. 2).

To correlate the experimental and calculated data (assuming  $\Delta S^\ddagger \sim 0$ ), we estimated the Gibbs energies for

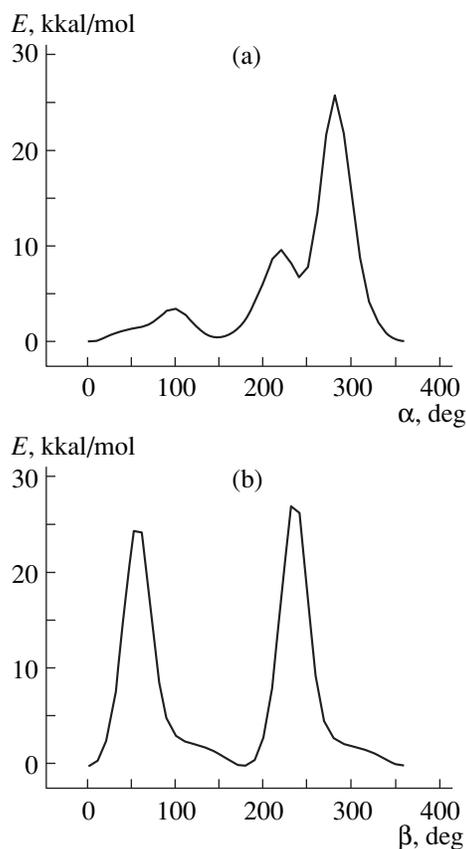
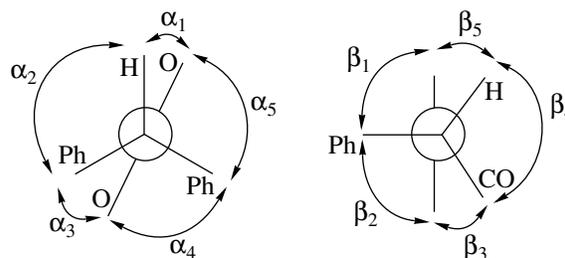


Fig. 2. Calculated energies of (a) retarded rotation 1 and (b) retarded rotation 2 vs. the angles of internal rotation.



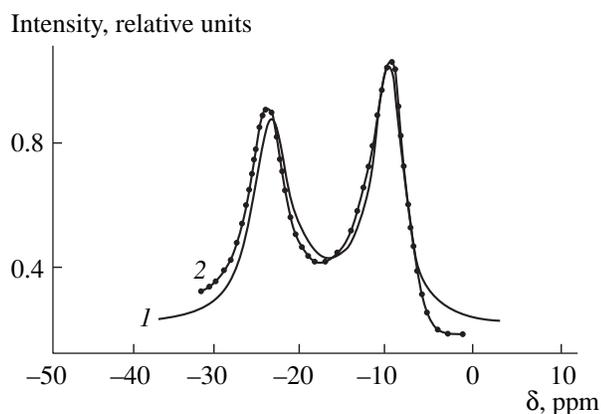
can be realized at the following torsion angles:

the *cis*–*trans* transition and the conformational isomerization of compound **I** using dynamic NMR data.

The calculations were performed by the Eyring equation at the coalescence point [15, 16]:

$$\Delta G_T^\ddagger = 19.14T_c[9.97 + \log(T_c/\Delta\delta)](\text{J/mol}),$$

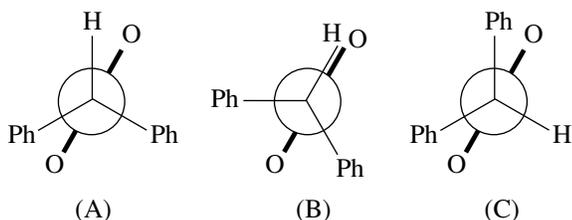
where  $T_c$  is the coalescence temperature and  $\Delta\delta$  is the difference between the chemical shifts of the signals from the two isomers. The coalescence point for sepa-



**Fig. 3.** (1) Theoretical and (2) calculated  $^1\text{H}$  NMR spectra for dynamic *cis*  $\rightleftharpoons$  *trans* equilibrium in a solution of  $[\text{Co}(\gamma\text{-Pic})_2(\text{Dfa})_2]$ .

ration of the *cis* and *trans* isomers (263 K) is higher than that for separation of the conformers (223 K). The energy barriers ( $\Delta G_T^\ddagger$ ) are equal to 13.0 and 10.3 kkal/mol, respectively (Fig. 3).

Comparison of the energies obtained from the conformational analysis and the NMR data allows one to draw the conclusion that the split of the signals from the diphenylacetate moiety is caused, first of all, by the presence of the *cis* and *trans* isomers in the solution and, second, by the presence of equilibrium conformers A, B, and C.



Note in conclusion that the experimental and theoretical energies of the conformational exchange show that when a slow intermolecular ligand exchange sets in (263 K), the slow exchange between the A, B, and C conformers has not yet been reached; it is only at 223 K

(and below) that the conditions for retarded rotation are reached for conformers separated by a barrier of 10 kkal/mol (Fig. 2b). In other words, while the phenyl radical in conformer C retards its rotation, in conformers A and B, the same radical continues to rotate.

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