Chemistry

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1964

SovietRxiv

Abstract

Full Text

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ON THE QUESTION OF FOUR-COORDINATE CHELATES WITH UNEQUAL LIGANDS

Usually four-coordinate intracomplex nonionic compounds contain two identical ligands bound by a metal atom. We became interested in the possibility of obtaining chelates in which the metal would bind two different ligands, in other words, chelates with unequal ligands.

The objects of investigation were compounds of structure (A), which contain two six-membered fused metallacycles:

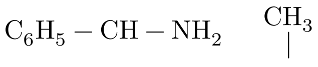
[[structural formula: salicylaldimine chelate with metal Me, substituents R_1 and R_2]]
(A)

Researchers, as a rule, deal with chelates in which R_1 and R_2 are residues of some one amine. We attempted, by the method of nascent reagents, to obtain from Schiff bases chelate compounds of structure (A), where $R_1 = CH_3-$, and $R_2 = C_6H_5-$ or $C_6H_5CH_2-$ or C_6H_5-CH-.

CH_3 |

In the X-ray diffraction patterns obtained, bands were found that are characteristic only of chelates in which $R_1 = R_2$; thus, in these cases as well the complex-formation reaction led to the production of a mechanical mixture of chelates with equal ligands (for example, $R_1 = R_2 = CH_3-$ and $R_1 = R_2 = C_6H_5CH_2-$). We then turned to a compound in which the difference between the initial salicylalimines, more precisely between the amine residues R_1 and R_2, consisted in their configuration.

α-Phenylethylamine was used,



$$C_6H_5-\underset{\substack{|\\ CH_3}}{CH}-NH_2 \qquad (I)$$

capable of existing in two forms: levorotatory (L) and dextrorotatory (D). Usually, after resolution with d-tartaric acid, α-phenylethylamine has $[\alpha]_D^{20} =$

−41.1°. We took amine I with $[\alpha]_D^{20} = -24°$, containing ∼ 60% of the pure *L*-form and ∼ 40% of racemate (20% *L* and 20% *D*). From it we obtained salicylal-α-phenylethylimine

[[structural formula: salicylal-α-phenylethylimine]]

$$\mathrm{HO{-}C_6H_4{-}CH{=}N{-}{}^*CH(C_6H_5)(CH_3)} \tag{II}$$

If copper acetate is added to a methanolic solution of this Schiff base II in the amount necessary to bind into the chelate ∼ 40% of salicylalimine II, the following cases are possible: 1) a mechanical mixture of two chelates with equal ligands, $R_1 = R_2 = L$-phenylethyl, $R_1 = R_2 = D$-phenylethyl, is obtained in a ratio proportional to the content of the *L*- and *D*-forms in the amine taken; 2) a chelate with unequal ligands is formed, $R_1 = L$-phenylethyl, $R_2 = D$-phenylethyl; 3) chelates with equal ligands are isolated, which upon crystallization form mixed racemic crystals.

In the first case, the angle of rotation of I, isolated from the remaining unbound II, should not differ from the angle of rotation of the initial amine I. In the second and third cases it should increase, since the racemic portion of the amine taken is bound either as a result of complex formation (case 2), or is removed from the reaction sphere through crystallization (case 3). The results of the investigations carried out are given in Table 1.

Table 1

Data on the formation of chelates with mixed (*L*, *D*)-salicylal-α-phenylethylimine

No. of experiment	α-phenylethylamine	salicylaldehyde	copper acetate	nickel acetate	$[\alpha]_D^{20}$ of the initial amine	$[\alpha]_D^{20}$ of the amine isolated from unbound Schiff base	$[\alpha]_D^{20}$ of the amine isolated from the formed chelate
1	0.05	0.05	0.003		−21.1°	−25.3°	
2	0.05	0.05	0.005		−23.9°	−33.7°	
3	0.07	0.07	0.016		−21.1°	−40.8°	−1.0°
4	0.07	0.07	0.012		+27.3°	+41.1°	
5	0.07	0.07		0.01	+27.3°	+38.1°	

The data obtained indicate that this method can serve as a method for estimating the degree of optical purity of the initial amine. Amines that have not been completely resolved can be "purified,"i.e., their angle of rotation can be increased. However, it cannot be concluded from this which case, the second or the third, is involved here. To answer this question we carried out the complex-formation reaction without isolating the chelate as a precipitate.

Upon gradual addition of an exactly known amount of copper acetate to a solution of mixed L, D-salicylal-α-phenylethylimine containing an excess of the L-form, a change in the angle of rotation of the solution was observed from the very beginning. This is associated with the appearance in the solution of optically active chelate molecules (for salicylal-(−)-α-phenylethylimine $[M]_{546\,\mathrm{m}\mu} = +484^\circ$, for bis-(salicylal-(−)-α-phenylethylimine)-copper $[M]_{546\,\mathrm{m}\mu} = -226^\circ$). Consequently, such polarimetric titration shows that a mixture of chelates with equal-pair ligands is formed in solution in a ratio proportional to the content of the L- and D-forms in the amine taken.

On crystallization the racemic modification precipitates, i.e., mixed crystals in which the levorotatory and dextrorotatory chelate molecules are present in equal amounts.

Cases of the formation of such racemic modifications in the example of complex compounds have already been noted in the literature[3]. Gradually the solution is enriched in the optically active form that had been taken in excess. Owing to the ability of the chelates of the type considered to form racemic modifications upon crystallization, it is possible completely to separate the optically active portion of the amine from its racemate.

An attempt to carry out an analogous separation using the formation of bis-(α-phenylethyldithiocarbamate)-nickel did not give positive results.

On the basis of the foregoing it may be concluded that the most energetically favorable chelate compounds of type (A) are those in which $R_1 = R_2$, i.e., chelates with equal-pair ligands.

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Received
16 XI 1963

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Note: Figure translations are in progress. See original paper for figures.