Complexes of Diformazyl Derivatives of Dibenzo-18-crown-6 (I-VII) with Transition Metals (VIII-XIX) (Table 2). A 0.005-mole sample of the transition metal salt in 3 ml of water was added to a hot solution of 0.002 mole of I-VII in 200 ml of methanol, and the reaction mixture was heated on a water bath at 65-70°C for 1 h and allowed to stand overnight. The precipitate was removed by filtration, washed with 3% acetic acid and water, and dried *in vacuo*. The products were obtained in 56-75% yields.

Complexes of Diformazyl Derivatives of Dibenzo-18-crown-6 with Transition and Alakli or Alkaline-Earth Metals (XX-XXVI) (Table 3). A 0.002-mole sample of complex VIII-XIX and 0.002 mole of the salt of an alkali or alkaline earth metal were dissolved by heating in DMF, and the reaction mixture was heated on a water bath for 10-15 min. The solvent was removed by distillation, and the residue was dried *in vacuo*. The yields were quantitative.

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CRYSTAL AND MOLECULAR STRUCTURE OF CHELATE COMPOUNDS OF Co(II) AND Ni(II) WITH (2-MERCAPTO-5-ETHYL-3-THENYLIDENE)CYCLOHEXYLAMINE

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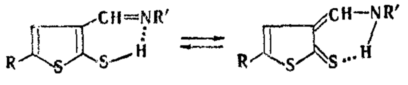
UDC 547.736:541.732'49

Chelate compounds of Co(II) and Ni(II) with (2-mercapto-5-ethyl-3-thenylidene)-cyclohexylamine were subjected to x-ray diffraction analysis. It was established that the investigated chelates are isostructural and that the metal atoms are tetrahedrally coordinated. It is shown that an intermediate distribution of the multiple bonds is realized in the examined chelate compound, just as in the starting ligand, and that their structures cannot be described within the framework of canonical structures.

A study of the tautomerism of mercaptoaldimines of the thiophene series — new ligands of the I type — has shown that in solutions of these compounds the equilibria are shifted virtually completely to favor the thionamine form with an intramolecular NH...S hydrogen bond [1], whereas in the crystalline state the distribution of the bond lengths constitute evidence for the contribution of both tautomeric forms and the absence of preponderance of one of them [2].



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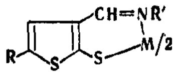

II, III

R=H, alkyl R'=*cyclo*-C_6H_{11}; II M=Co(II); III M=Ni(II)

In this connection, it seemed of interest to study the structures of the chelate compounds formed by these ligands to obtain a solution to the problem as to the presence or absence of tautomeric forms in the metal complexes and the effect of complexing on the stereochemistry of the ligand.

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TABLE 1. Coordinates of the Atoms in the II Molecule

Atom	X	Y	Z	Atom	X	Y	Z
	Nonhydrogen atoms ($\cdot 10^4$)				Hydrogen atoms ($\cdot 10^3$)		
Co	1962 (0)	1467 (0)	82 (0)	3-H	103	−126	247
S_1	1311 (1)	1829 (2)	1845 (2)	5-H	183	−92	178
S_2	474 (1)	827 (2)	2810 (2)	6-H	242	−75	68
S_3	2667 (1)	2338 (2)	1116 (1)	7-H	307	48	144
S_4	3567 (1)	2957 (2)	−34 (2)	71-H	283	−37	216
N_1	2057 (2)	231 (4)	1101 (4)	8-H	345	−128	108
N_2	1825 (2)	1765 (4)	−487 (4)	81-H	385	−52	165
C_1	491 (4)	856 (5)	2159 (5)	9-H	377	40	26
C_2	945 (4)	−244 (6)	2945 (6)	91-H	405	−65	−1
C_3	1257 (3)	−610 (5)	2484 (6)	10-H	333	−22	−119
C_4	1257 (3)	35 (5)	2044 (5)	101-H	311	−115	−53
C_5	1743 (3)	−258 (5)	1584 (5)	11-H	277	75	−17
C_6	2532 (4)	−250 (5)	761 (5)	111-H	235	−8	−67
C_7	2975 (4)	−118 (6)	1477 (6)	12-H	−17	−19	389
C_8	3513 (4)	−627 (7)	1147 (9)	121-H	−25	−96	295
C_9	3681 (4)	−298 (7)	217 (8)	16-H	331	297	−120
C_{10}	3225 (4)	−451 (6)	−498 (6)	18-H	203	218	−185
C_{11}	2686 (4)	52 (6)	−188 (6)	19-H	142	153	−171
C_{12}	39 (4)	−694 (7)	3469 (7)	20-H	107	74	24
C_{13}	219 (5)	−738 (10)	4426 (12)	201-H	143	30	−96
C_{14}	2933 (3)	2530 (5)	38 (5)	21-H	41	−6	−47
C_{15}	3545 (4)	3015 (6)	−1209 (6)	211-H	55	60	−155
C_{16}	3049 (3)	2708 (5)	−1520 (6)	22-H	8	133	13
C_{17}	2706 (3)	2419 (5)	−805 (5)	221-H	−30	116	−93
C_{18}	2166 (3)	2135 (5)	−1038 (5)	23-H	39	203	−177
C_{19}	1291 (3)	1587 (5)	−909 (5)	231-H	6	259	−68
C_{20}	1087 (3)	714 (5)	−525 (6)	24-H	110	296	−52
C_{21}	506 (3)	546 (5)	−924 (6)	241-H	55	242	−113
C_{22}	107 (3)	1288 (5)	−641 (6)	25-H	441	329	−140
C_{23}	324 (3)	2143 (5)	−1024 (6)	251-H	395	416	−175
C_{24}	904 (3)	2326 (5)	−664 (5)				
C_{25}	4014 (4)	3443 (7)	−1737 (7)				
C_{26}	4008 (4)	3279 (7)	−2715 (7)				

TABLE 2. Coordinates of the Nonhydrogen Atoms in the III Molecule ($\cdot 10^4$)

Atom	X	Y	Z	Atom	X	Y	Z
Ni	1884 (1)	1710 (2)	1010 (2)	C_{11}	2574 (5)	−252 (7)	−16 (9)
S_1	1156 (2)	1858 (3)	1960 (3)	C_{12}	171 (5)	−1056 (7)	3555 (9)
S_2	450 (2)	615 (3)	2962 (3)	C_{13}	351 (5)	−1100 (7)	4512 (9)
S_3	2610 (2)	2540 (3)	1289 (3)	C_{14}	2934 (4)	2677 (6)	228 (7)
S_4	3581 (2)	3074 (3)	160 (3)	C_{15}	3617 (4)	3013 (6)	−1037 (7)
N_1	2114 (3)	533 (5)	1223 (5)	C_{16}	3136 (4)	2689 (6)	−1376 (7)
N_2	1841 (3)	1798 (5)	−382 (5)	C_{17}	2733 (4)	2456 (6)	−670 (7)
C_1	1034 (4)	850 (6)	2319 (7)	C_{18}	2196 (4)	2162 (6)	−913 (7)
C_2	547 (4)	−431 (6)	3073 (7)	C_{19}	1287 (5)	1633 (7)	−829 (9)
C_3	1065 (4)	−633 (6)	2578 (7)	C_{20}	859 (5)	2330 (7)	−636 (9)
C_4	1315 (4)	80 (6)	2115 (7)	C_{21}	303 (5)	2072 (7)	−1088 (9)
C_5	1845 (4)	−60 (6)	1640 (7)	C_{22}	87 (5)	1198 (7)	−726 (9)
C_6	2670 (5)	325 (7)	796 (9)	C_{23}	521 (5)	557 (7)	−980 (9)
C_7	3026 (5)	−14 (7)	1610 (9)	C_{24}	1114 (5)	720 (7)	−494 (9)
C_8	3627 (5)	−121 (7)	1130 (9)	C_{25}	4131 (5)	3353 (7)	−1548 (9)
C_9	3585 (5)	−667 (7)	314 (9)	C_{26}	4098 (5)	3185 (7)	−2610 (9)
C_{10}	3188 (5)	−411 (7)	−422 (9)				

TABLE 3. Geometry of the Coordination Polyhedron in Complexes II and III

Bond	d, Å		Angle	ω, deg	
	II	III		II	III
$M-S_1$	2,271 (3)	2,244 (5)	S1MS3	105,9 (1)	115,6 (2)
$M-N_1$	1,995 (6)	2,010 (8)	S1MN1	99,8 (1)	103,3 (4)
$M-S_3$	2,258 (3)	2,255 (5)	S1MN2	117,2 (1)	123,9 (4)
$M-N_1$	2,010 (6)	2,010 (8)	S3MN1	117,0 (1)	109,2 (4)
			S3MN2	101,1 (1)	99,9 (4)
			N1MN2	116,1 (2)	104,0 (6)

TABLE 4. Bond Lengths in the II Structure

Bond	d, Å	Bond	d, Å	Bond	d, Å
S_1—C_1	1,707 (8)	C_9—C_{10}	1,56 (1)	C_{18}—N_2	1,31 (1)
S_2—C_1	1,749 (8)	C_{10}—C_{11}	1,61 (1)	N_2—C_{19}	1,49 (1)
S_2—C_2	1,692 (9)	C_6—C_{11}	1,52 (1)	C_{19}—C_{20}	1,56 (1)
C_2—C_3	1,43 (1)	C_2—C_{12}	1,53 (1)	C_{20}—C_{21}	1,58 (1)
C_3—C_4	1,43 (1)	C_{12}—C_{13}	1,45 (1)	C_{21}—C_{22}	1,58 (1)
C_1—C_4	1,38 (1)	S_3—C_{14}	1,740 (8)	C_{22}—C_{23}	1,55 (1)
C_4—C_5	1,45 (1)	S_4—C_{14}	1,711 (8)	C_{23}—C_{24}	1,56 (1)
C_5—N_1	1,30 (1)	S_4—C_{15}	1,728 (9)	C_{19}—C_{24}	1,55 (1)
N_1—C_6	1,48 (1)	C_{15}—C_{16}	1,40 (1)	C_{15}—C_{25}	1,55 (1)
C_6—C_7	1,53 (1)	C_{16}—C_{17}	1,42 (1)	C_{25}—C_{26}	1,46 (1)
C_7—C_8	1,62 (1)	C_{14}—C_{17}	1,37 (1)		
C_8—C_9	1,52 (1)	C_{17}—C_{18}	1,45 (1)		

TABLE 5. Bond Lengths in the III Structure

Bond	d, Å	Bond	d, Å	Bond	d, Å
S_1—C_1	1,74 (1)	C_9—C_{10}	1,49 (2)	C_{18}—N_2	1,29 (2)
S_2—C_1	1,73 (1)	C_{10}—C_{11}	1,61 (2)	N_2—C_{19}	1,51 (2)
S_2—C_2	1,73 (1)	C_6—C_{11}	1,52 (2)	C_{19}—C_{20}	1,56 (2)
C_2—C_3	1,47 (2)	C_2—C_{12}	1,53 (2)	C_{20}—C_{21}	1,55 (2)
C_3—C_4	1,47 (2)	C_{12}—C_{13}	1,45 (2)	C_{21}—C_{22}	1,60 (2)
C_1—C_4	1,46 (2)	S_3—C_{14}	1,73 (2)	C_{22}—C_{23}	1,53 (2)
C_4—C_5	1,47 (2)	S_4—C_{14}	1,70 (2)	C_{23}—C_{24}	1,62 (2)
C_5—N_1	1,31 (2)	S_4—C_{15}	1,72 (2)	C_{19}—C_{24}	1,62 (2)
N_1—C_6	1,51 (2)	C_{15}—C_{16}	1,37 (2)	C_{15}—C_{25}	1,55 (2)
C_6—C_7	1,55 (2)	C_{16}—C_{17}	1,46 (2)	C_{25}—C_{26}	1,55 (2)
C_7—C_8	1,62 (2)	C_{14}—C_{17}	1,43 (2)		
C_8—C_9	1,48 (2)	C_{17}—C_{18}	1,43 (2)		

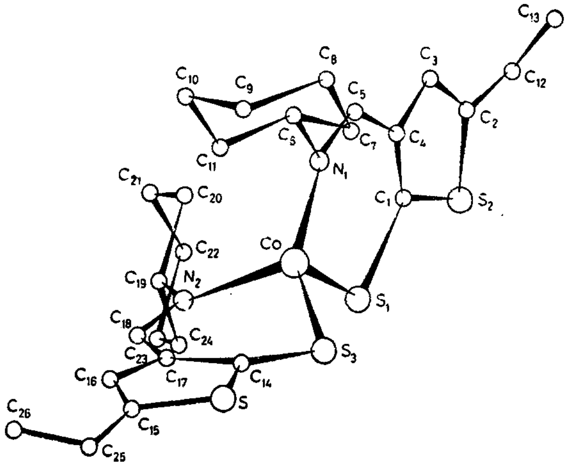

Fig. 1. Geometry of the II molecule.

In the present paper we present the results of an x-ray diffraction study of two chelate compounds of (2-mercapto-5-ethyl-3-thenylidene)cyclohexylamine with Co(II) and Ni(II) (II and III, respectively). Single crystals of complexes II and III suitable for recording were obtained from solutions in acetone. Complexes II and III have rhombic syngony with space group Pbca and z = 8. The lattice parameters are as follows: For II, a = 24.772(4), b = 15.686(3), c = 14.675(2) Å, ρ_{meas} = 1.31 g/cm³, and ρ_{calc} = 1.318 g/cm³; for III, a = 24.215(5), b = 16.310(3), c = 14.365 Å, ρ_{meas} = 1.32 g/cm³, and ρ_{calc} = 1.319 g/cm³. The specific densities were measured by the flotation method in an aqueous solution of zinc chloride.

The experimental data were obtained with a Syntex PI automatic diffractometer with λMo K_α emission, a graphite monochromator, $\theta/2\theta$ scanning, $\sin\theta/\lambda_{max}$ = 0.78 and 0.65, and 1944 and 1057 independent reflections, respectively, with $I \geq 3\sigma$ (I).

The structures were elucidated by the heavy-atom method with subsequent refinement by the method of least squares within the isotropic approximation by means of the Rentgen-70 program [3]. In the case of complex II refinement was continued within the anisotropic approximation for the nonhydrogen atoms by means of the Kristall program [4]. The coordinates of 30 of the 36 hydrogen atoms for II were localized from differential syntheses of the electron density and were refined by the method of least squares within the isotropic approximation with fixed B_j values. The final R values were 0.049 and 0.098 for complexes II and III, respectively.

The coordinates of the atoms for complexes II and III are presented in Tables 1 and 2. The heat factors can be obtained from the authors.

The study showed that complexes II and III are isostructural. The coordination polyhedron is a somewhat distorted tetrahedron with two sulfur atoms and two nitrogen atoms from two bidentate ligands at the apexes. The angles between the coordination planes are close for both compounds and amount to 85°. The bond lengths and angles in the II and III polyhedra are presented in Table 3. From a comparison of the bond angles it may be concluded that the tetrahedron is less distorted in complex II than in complex III. One's attention is directed to the different ratios between the SMS and NMN angles in the two compounds. The angular characteristics of the polyhedron in the II crystal are close to the corresponding values in the previously investigated structure of the complex of Co(II) with a related tridentate ligand, viz., 2-mercapto-5-ethyl-3-thenylidene-α-aminopyridine [5].

The conformation of the II molecule with the designation of the atoms is shown in Fig. 1. The bond lengths are presented in Tables 4 and 5. All of the interatomic distances in the II and III complexes (except for the C-C distances in the cyclohexyl rings) coincide in the two crystallographically independent halves of the molecules within the limits of 2-3σ for different bonds.

The lengths of the S—C bonds of the thiophene fragments differ only slightly from the corresponding values observed for thiophene (1.74 Å) [6] and free ligand I (R = H) (1.72 and 1.74 Å) [2]. The exocyclic S—C bonds differ little from thiophene bonds and somewhat exceed the length of the analogous bond in the free ligand. The interatomic C—C distances in the heterorings indicate the absence of the localization of the double bonds that is observed in free thiophene. The exocyclic C—C bonds (the average value with respect to the two structures) are elongated as compared with the free ligand (1.40 Å), while the C—N bonds within the rings coincide (within the limits of the experimental error) with the bonds in the indicated ligand (1.284 Å).

Starting from the corresponding interatomic distances, the S—C, C—N, and C—C bonds in chelates II and III, as in ligand I [2], can be interpreted as intermediate between single and double bonds with a somewhat different degree of delocalization in each individual case, and this indicates a tendency for conjugation of the bonds over the entire molecule. This makes it impossible to assign it within the framework of one of the canonical forms and enables us to conclude that an intermediate form with delocalized bonds is realized.

The lengths of the C—C bonds in the cyclohexyl rings have considerable scatter, as in structure I. The ring exists in a chair conformation with torsion angles that are customary for this conformation. The lengths of the exocyclic C—N bond coincide with the standard values (1.47 Å).

The metallocycles in complexes II and III are bent along the S...N line. The deviations of the Co atom from the plane of the ligand in chelate II is 0.498 and 0.363 Å for the two halves of the molecule. The ligand in all cases has a planar structure, and the maximum deviation from planarity does not exceed 0.08 Å (the N atoms). A similar situation is also observed in the case of the free ligand, which also has a planar structure with the greatest deviation of the N atoms from the plane of the thiophene rings.

All of the intermolecular distances in the crystal exceed the sums of the van der Walls radii of the corresponding atoms.

Thus the data obtained constitute evidence that replacement of the hydrogen atom in ligand I by a metal atom (Co, Ni) does not entail substantial changes in the geometry of the molecule.

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INVESTIGATION OF THE REACTION OF 1-METHYL-2,5-DICHLORO-3,4-DIFORMYLPYRROLE WITH AMINES

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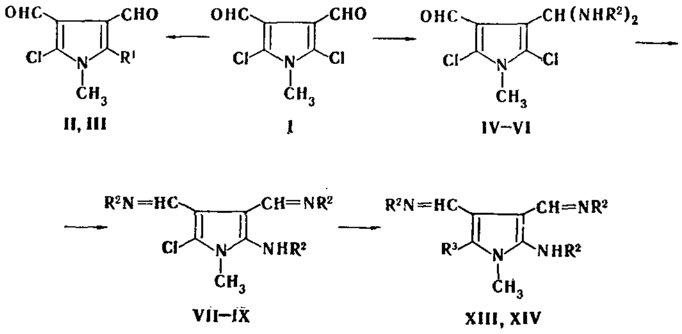
UDC 547.743.4

The reaction of 1-methyl-2,5-dichloro-3,4-diformylpyrrole with amines of the aliphatic series leads to products of replacement of one chlorine atom. With aromatic amines the reaction takes place at one of the formyl groups to give aminals. The latter in the presence of excess amine readily give bisazomethines of 1-methyl-2-chloro-5-arylamino-3,4-diformylpyrrole, which can also be obtained directly by the reaction of dichlorodiformylpyrrole with arylamines. It is shown that in this case one of the formyl groups and the adjacent chlorine atom react initially, after which the second formyl group reacts. The chlorine atom in bisazomethines of 1-methyl-2-chloro-5-arylamino-3,4-diformylpyrrole has high nucleophilic lability and is easily replaced by a hydroxy group or a piperidine residue.

During a study of the properties of 1-methyl-2,5-dichloro-3,4-diformylpyrrole (I) [1] it was observed that its reaction with amines proceeds in a rather complex manner and that the reaction pathway depends to a considerable extent on the nature of the amine. Thus the reaction does not occur with methylamine, cyclohexylamine, and piperidine under mild conditions (60% aqueous alcohol, 20°C), whereas primarily products of replacement of one chlorine atom by an amine residue, viz., II and III, are formed under severe conditions.

In contrast to alkylamines, the dichlorodiformylpyrrole reacts with aromatic amines even under mild conditions (aqueous alcohol, 20°C) to give aminals IV-VI.



II R^1= piperidino III R^1= cyclohexylamino IV, VII R^2=C_6H_5; V, VIII R^2=p-$CH_3OC_6H_4$; VI, IX R^2=p-BrC_6H_4; XIV R^2=C_6H_5, R^3= piperidino XIII R^2=C_6H_5, R^3=OH

Aminals of aromatic and heterocyclic aldehydes are usually obtained in the reaction with strongly basic amines [2-5]. For example, brief heating of benzaldehyde in an aqueous solu-

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Lensovet Leningrad Technological Institute, Leningrad 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1489-1493, November, 1981. Original article submitted December 2, 1980.

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