SYNTHESIS AND CRYSTAL STRUCTURE OF THE MOLECULES OF 1-(2-BENZOTHIAZOLYL)-3,5-DIMETHYLPYRAZOLE $C_{12}H_{11}N_3S$ AND DIOXODICHLORO[1-(2-BENZOTHIAZOLYL)-3,5-DIMETHYLPYRAZOLE]MOLYBDENUM(VI) $[MoO_2(C_{12}H_{11}N_3S)Cl_2]$

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The synthesis and x-ray crystallographic investigation of the molecule of 1-(2-benzothiazolyl)-3,5-dimethylpyrazole, L (I), and the molecular complex $MoO_2Cl_2 \cdot L$ (II) were undertaken [diffractometer, λMo, direct method for (I), heavy atom method for (II), R = 0.080 in 468 reflections for (I), R = 0.046 in 1446 reflections for (II)]. The crystals of (I) are rhombic with a = 17.797, b = 10.836, c = 12.172 Å, d_{det} = 1.38 g/cm^3, Z = 8, space group Pcab; the crystals of (II) are monoclinic with a = 10.305, b = 11.927, c = 12.825 Å, β = 92.53°, d_{det} = 1.81, Z = 4, space group $P2_1/n$. The molecule of L in (I) has the s-trans conformation. During complexation with molybdenum the benzothiazole ring of the ligand L in (II) is rotated about the C(1)—N(2) bond by ~180°. In the complex (II) the Mo atom has a distorted octahedral coordination with the cis structure for the dioxo group, as in other complexes of the d^0 metals of groups V-VIII. The N(1) atom of the benzothiazole and N(3) atom of the pyrazole ring of the bidentate ligand L occupy the trans positions to the oxo atoms. The five-membered metallocycle MoN_3C has the envelope conformation with the Mo "corner" bent from the plane of the N(1-3) and C(1) atoms by 0.132 Å. The average bond lengths in (II) are: Mo—O 1.685, Mo—Cl 2.357, Mo—N 2.310 Å. As usual, the Mo—N bonds are elongated as a result of the trans effect of the multiply bonded oxo ligands.

In a systematic study of the complexing characteristics and structure of the dioxo compounds of molybdenum(VI) and complexes based on MoO_2Cl_2, in particular, the product from the condensation of acetylacetone and 2-hydrazinobenzothiazole L (I) and the molecular complex $MoO_2Cl_2 \cdot L$ (II) were synthesized and investigated by x-ray crystallographic analysis.

EXPERIMENTAL

To obtain 1-(2-benzothiazolyl)-3,5-dimethylpyrazole we mixed equimolar amounts of acetylacetone and 2-hydrazinobenzothiazole in benzene in a reaction flask fitted with a Dean—Stark tube. We then added several crystals of p-toluenesulfonic acid as catalyst and boiled the mixture on a water bath for 2 h. The yellowish crystals which separated after cooling were recrystallized twice from benzene; mp 143-144°C. Found %: C 62.75; H 4.80; N 18.27; S 14.06. $C_{12}H_{11}N_3S$ Calculated %: C 62.86; H 4.84; N 18.32; S 13.98.

The complex $MoO_2Cl_2 \cdot L$ was obtained in the following way. To 25 ml of a solution containing 0.001 mole of MoO_2Cl_2 in absolute ethyl acetate we added with stirring 0.001 mole of the ligand in the same solvent. The mixture

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TABLE 1. The Crystallographic Data and Experimental Characteristics for Compounds (I) and (II)

Lattice parameter	I	II	Parameter	I	II
a, Å	17,797(3)	10,305(2)	μ_{M_0}, cm^{-1}	2,6	12,9
b, Å	10,836(3)	11,927(2)	Sp. group	$P\,cab$	$P2_1/n$
c, Å	12,172(2)	12,825(3)	$2\theta_{max}$, deg	40	50
β, deg	90	92,53(2)	N^*_{tot}	968	2154
V, Å^3	2215,2(8)	1574,7(6)	N, $I > 1{,}96\sigma(I)$	468	1446
d_{det}, g/cm^3	1,38(3)	1,81(1)	R_F	0,080	0,046
d_{calc}, g/cm^3	1,385(3)	1,807(2)	$R^{\dagger}_w$	0,045	0,026
Z	8	4	$f^{\ddagger}$	1,524	1,455
			Q^{**}	145	190

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*N is the number of reflections.

†$1/w = \sigma(F)^2 + (0{,}0 \cdot F_{\partial expt})^2$, $F_{expt} \geq 3.92\sigma(F)$.

‡$f = [\Sigma(|F_{det} - F_{calc}|/\sigma(F))^2/(N - W)]^{1/2}$.

**Q is the number of refined parameters.

TABLE 2. The Atomic Coordinates (in unit cell fractions) in the Structure of (I)

Atom	x	y	z	B_{eq} (B_H)
S(1)	0,2978(3)	0,3696(4)	0,4174(3)	3,6
N(1)	0,3023(8)	0,3192(13)	0,2073(9)	3,4
N(2)	0,3890(7)	0,4837(13)	0,2636(11)	2,8
N(3)	0,4218(8)	0,5336(14)	0,3572(10)	3,3
C(1)	0,4218(8)	0,5336(14)	0,3518(10)	3,0
C(2)	0,2349(9)	0,2582(14)	0,3670(11)	2,5
C(3)	0,2477(8)	0,2451(15)	0,2538(13)	2,4
C(4)	0,2040(11)	0,1544(17)	0,1978(11)	4,0
C(5)	0,1503(10)	0,0794(15)	0,2556(16)	4,1
C(6)	0,1386(9)	0,0989(17)	0,3680(14)	4,5
C(7)	0,1806(10)	0,1864(15)	0,4257(11)	3,6
C(8)	0,4678(9)	0,6202(21)	0,3203(16)	4,3
C(9)	0,4654(10)	0,6271(19)	0,2047(15)	4,1
C(10)	0,4137(11)	0,5374(18)	0,1692(12)	3,4
C(11)	0,5168(10)	0,6994(15)	0,3937(11)	4,8
C(12)	0,3838(8)	0,5069(16)	0,0584(10)	4,6
H(4)	0,210	0,143	0,113	5
H(5)	0,119	0,007	0,217	5
H(6)	0,098	0,046	0,412	5
H(7)	0,172	0,201	0,510	5
H(9)	0,497	0,689	0,155	5
H(111)	0,576	0,719	0,366	5
H(112)	0,521	0,653	0,471	5
H(113)	0,486	0,782	0,406	5
H(121)	0,412	0,547	−0,011	5
H(122)	0,324	0,529	0,055	5
H(123)	0,390	0,410	0,049	5

TABLE 3. The Atomic Coordinates (in unit cell fractions) in the Structure of (II)

Atom	x	y	z	B_{eq} (B_H)
Mo(1)	0,11148(6)	0,20469(6)	0,19893(5)	3,21
Cl(1)	—0,0604(2)	0,2404(2)	0,0757(1)	4,5
Cl(2)	0,2187(2)	0,1696(2)	0,3615(1)	5,4
O(1)	0,1973(5)	0,3216(4)	0,1734(3)	4,3
O(2)	0,1809(5)	0,1023(4)	0,1308(3)	4,6
S(1)	—0,2146(2)	0,2975(2)	0,4393(1)	3,8
N(1)	—0,0347(5)	0,2925(5)	0,3050(4)	2,7
N(2)	—0,1218(6)	0,1173(5)	0,3316(4)	2,9
N(3)	—0,0329(6)	0,0782(5)	0,2632(4)	3,2
C(1)	—0,1164(7)	0,2320(6)	0,3536(5)	2,6
C(2)	—0,1429(7)	0,4243(6)	0,4057(5)	2,8
C(3)	—0,0480(7)	0,4062(6)	0,3340(5)	2,8
C(4)	0,0229(7)	0,4967(7)	0,2962(5)	3,7
C(5)	—0,0054(8)	0,6011(6)	0,3326(6)	3,9
C(6)	—0,1029(8)	0,6183(6)	0,4046(6)	4,2
C(7)	—0,1721(7)	0,5302(6)	0,4425(6)	3,6
C(8)	—0,0556(8)	—0,0313(7)	0,2259(6)	3,5
C(9)	—0,1591(8)	—0,0620(6)	0,3198(6)	3,6
C(10)	—0,1995(7)	0,0314(7)	0,3662(5)	3,1
C(11)	0,0226(8)	—0,1046(6)	0,1899(6)	5,0
C(12)	—0,3071(8)	0,0482(7)	0,4404(6)	5,1
H(4)	0,097	0,484	0,240	5
H(5)	0,048	0,672	0,306	5
H(6)	—0,125	0,703	0,428	5
H(7)	—0,244	0,541	0,501	5
H(9)	—0,200	—0,145	0,325	5
H(111)	0,019	0,103	0,872	5
H(112)	0,886	0,074	0,841	5
H(113)	0,998	0,192	0,794	5
H(121)	0,738	0,053	0,497	5
H(122)	0,372	0,028	0,561	5
H(123)	0,650	0,100	0,425	5

TABLE 4. The Bond Angles ω (deg) in the Structure of (II) (not given in Fig. 3)

Angle	ω	Angle	ω
Cl(1)MoCl(2)	159,15(8)	O(2)MoN(3)	90,4(2)
Cl(1)MoO(1)	96,0(2)	N(1)MoN(3)	68,9(2)
Cl(1)MoO(2)	96,1(2)	MoN(1)C(3)	131,3(4)
Cl(1)MoN(1)	79,9(1)	C(1)N(2)C(10)	132,7(6)
Cl(1)MoN(3)	83,1(2)	MoN(3)C(8)	104,9(6)
Cl(2)MoO(1)	95,1(2)	S(1)C(1)N(2)	123,8(5)
Cl(2)MoO(2)	96,1(2)	S(1)C(2)C(7)	127,3(6)
Cl(2)MoN(1)	81,5(1)	N(1)C(3)C(4)	126,1(6)
Cl(2)MoN(3)	81,5(2)	N(3)C(8)C(11)	121,4(7)
O(1)MoO(2)	105,1(2)	C(9)C(8)C(11)	128,3(7)
O(1)MoN(1)	95,7(2)	N(2)C(10)C(12)	123,8(6)
O(1)MoN(3)	164,5(2)	C(9)C(10)C(12)	130,1(7)
O(2)MoN(1)	159,1(2)		

was left at room temperature to crystallize. The yellow crystals of $MoO_2Cl_2{\cdot}L$ were washed with ethyl acetate on a filter with a glass diaphragm and were dried in a vacuum drying cabinet; mp 258-259°C (decomp.). Found %: Mo 22.52; Cl 16.45. $MoO_2Cl_2{\cdot}L$. Calculated %: Mo 22.41; Cl 16.56. The IR spectra were recorded on a UR-20 spectrophotometer in the region of 2000-700 cm^{-1} for tablets with potassium bromide. The spectra of (I) and (II) contain the following characteristic absorption bands (ν, cm^{-1}): Ligand, 1600, 1580, 1543, 1448, 1410, 1387, 1363,

TABLE 5. The Departures of the Atoms from Certain Planes and the Angles between the Planes in the Structure of (I) [in the Structure of (II) in Parentheses]

Plane	Atoms and their departures, Å					
1	N(1) —0,043 (0,008)	C(1) 0,052 (—0,015)	N(2) 0,028 (0,015)	N(3) —0,036 —(0,008)	Mo * — (—0,132)	
2	N(2) 0,002 (—0,001)	N(3) —0,003 (0,001)	C(8) 0,002 (0,001)	C(9) —0,001 (—0,001)	C(10) —0,001 (0,002)	
3	N(1) 0,001 (—0,004)	C(1) 0,004 (0,010)	S(1) —0,006 (—0,009)	C(2) 0,008 (0,009)	C(3) —0,007 (—0,005)	
4	C(2) —0,011 (—0,001)	C(3) 0,002 (0,002)	C(4) 0,012 (0,001)	C(5) —0,017 (—0,005)	C(6) 0,009 (0,005)	C(7) 0,005 (—0,002)
5	Cl(1) (—0,029)	Cl(2) (—0,030)	O(1) (0,030)	N(3) (0,029)	Mo * 0,291	
6	Cl(1) (0,053)	Cl(2) (0,052)	O(2) (—0,052)	N(1) (—0,053)	Mo * (0,300)	
	Angles between the planes, deg: *1—2* 175,8(1,4), *1—3* 9,4(1,8), *3—4* 2,7(1,0), *5 — 6* (95,9).					

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*The asterisks denote the atoms not involved in the calculation of the plane.

1319, 1285, 1250, 1164, 1145, 1040, 973, 803, 774, 732; complex, 1578, 1523, 1449, 1380, 1362, 1285, 1252, 1163, 1141, 1087, 1064, 1020, 982, 950, 920, 769, 752, 730.

The experimental data for the x-ray investigations were obtained on a Syntex $P2_1$ four-circle automatic diffractometer with MoK_α radiation and a graphite monochromator. A correction was made for the anomalous scattering of the Mo, Cl, and S atoms in the structure of (II). All the calculations were conducted on a Nova-1200 minicomputer by means of the standard XTL programs. The crystallographic data and the principal experimental characteristics of the investigated compounds (I, II) are given in Table 1. The structure of (I) was determined by the direct method with 172 normalized structural amplitudes for which $E \geq 1.3$. The structure of (II) was solved by theheavy atom method. Both structures were refined by least-squares treatment in full-matrix anisotropic approximation for the nonhydrogen atoms. The hydrogen atoms in the structures of (I) and (II) were localized from Fourier difference syntheses and were included in the refinement at fixed positions (at the idealized positions with C—H distances of 1.05 Å for the atoms attached to the sp^2 hybridized carbon atoms) with fixed temperature factors B_H ~ 1 Å^2 $> B_C$ for the corresponding carbon atoms. The low accuracy in the investigation of the structure of (I) is determined by the small volume of experimental data.

The atomic coordinates and the temperature factors B_{eq} in the form $B_{eq} = 1/3(B_{11} + B_{22} + B_{33})$ and B_H for structures (I) and (II) respectively are given in Tables 2 and 3. The bond angles in the structure of (II) (not given in Fig. 3) are given in Table 4. The departures of the atoms from some planes and the angles between them in the structures of (I) and (II) are given in Table 5.

RESULTS AND DISCUSSION

Structure and Conformation of the Molecule of (I). The reaction of hydrazines with 1,3-dicarbonyl compounds is the classical method for the production of pyrazoles [1-3]. In this connection it could be expected that the reaction of acetylacetone with 2-hydrazinobenzothiazole would lead to the formation of 1-(2-benzothiazolyl)-3,5-dimethylpyrazole, which by analogy with α,α′-bipyridyl and other α,α′-nitrogen heterocycles should have the s-trans arrangement of the nitrogen atoms of the pyrazole and benzothiazole rings.

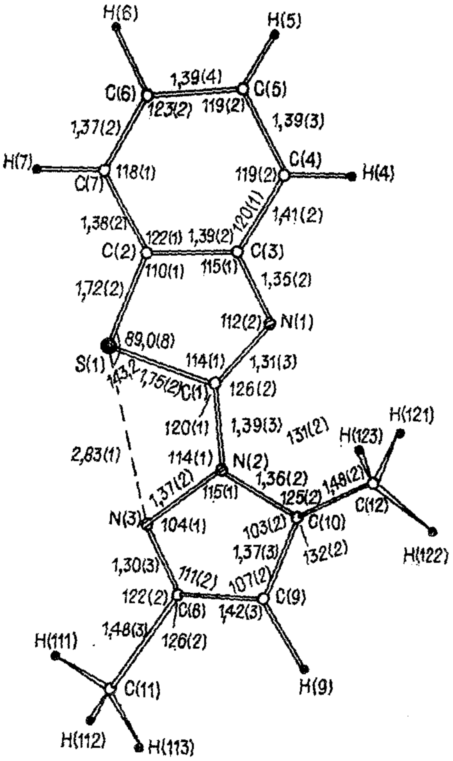


Fig. 1. The molecular structure of the 1-(2-benzothiazolyl)-3,5-dimethylpyrazole.

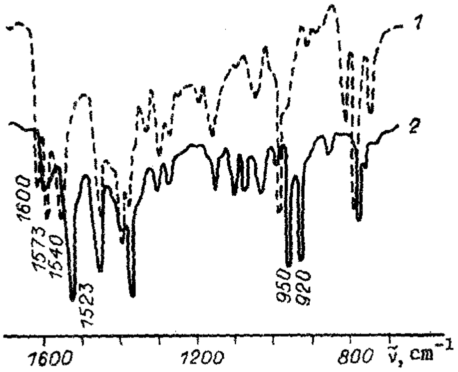
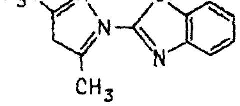


Fig. 2. The IR spectra of 1-(2-benzothiazolyl)-3,5-dimethylpyrazole L (1) and its molecular complex $MoO_2Cl_2{\cdot}L$ (2).



In fact, in the free molecule of (I) (Fig. 1) there is a short intramolecular S(1)···N(3) contact of 2.83 Å, which is substantially less than the sum of the van der Waals radii (3.35 Å according to Pauling [4]), bringing the configur-

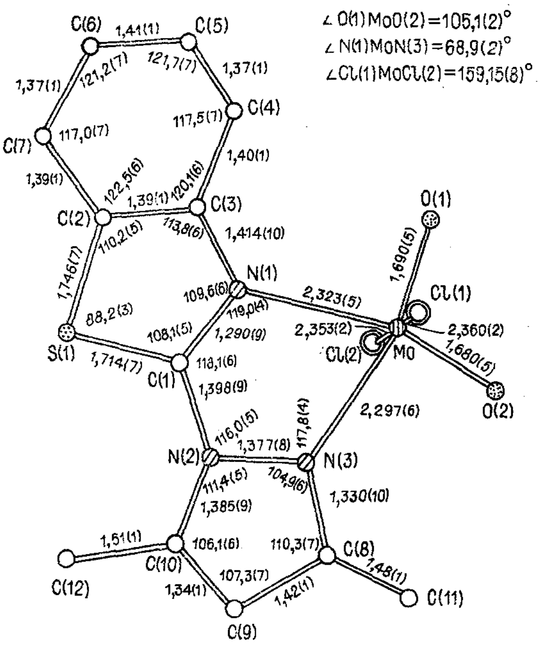
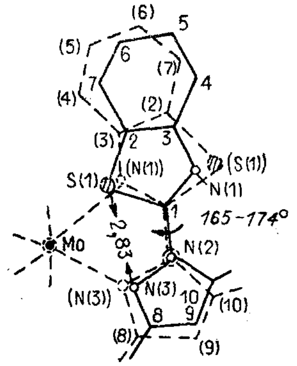


Fig. 3. The molecular structure of the dioxodichloro-1-(2-benzothiazolyl)-3,5-dimethylpyrazolemolybdenum (VI).



∠1-N(2)-N(3) = 114 (116°)
∠S(1)-1-N(2) = 120 (124°)
∠N(1)-1-N(2) = 126 (118°)
∠1-N(2)-10 = 131 (133°)
N(1)-3 = 1,34 (1,41 Å)
N(3)-8 = 1,29 (1,33 Å)

Fig. 4. The mutual arrangement of the 1-(2-benzothiazolyl)-3,5-dimethylpyrazole molecules in structures (I) and (II).

ation of the bonds about the sulfur atom to the typical approximately T-shaped configuration [N(3)S(1)C(2) angle 143°]. An intermolecular contact of similar type, somewhat larger in length (S···N 3.13 Å), was also found in the structure of benzo[1,2-c:3,4-c′]bis(1,2,5-thiadiazole) [5]. Intramolecular contacts of a similar type, corresponding to secondary S···N interactions, are typical of the heterocyclic molecules of thiazine derivatives [6]. In [6] a geometry was proposed, and an explanation was given for the nature of such interaction. We note that the secondary S···N interaction is an extremely important factor in the stabilization of the close to trans-planar configuration of the molecule (I); in the related molecules of α,α'-nitrogen bisheterocycles the departures from the plane are extremely significant [1-3].

Structure of the Coordination Unit in the Complex. Comparison of the vibrational spectra of the ligand with the spectrum of the complex (Fig. 2) shows that a large part of the principal absorption bands of the ligand in the region of the pulsation (700-1000 cm^{-1}) and vibration (1000-1450 cm^{-1}) oscillations [7,8] are shifted little during complex formation, and this demonstrates the closeness of the electronic structures of the azole rings in the coordinated and free states [9]. The largest shifts of the bands during complex formation are observed in the region of the frequencies for the stretching vibrations of the heterocycles (1450-1700 cm^{-1}), and this indicates that the pyrazole and benzothiazole rings of the ligand are included in the coordination through the nitrogen atoms. In the spectrum of thecomplex there is a strong doublet at 920 and 950 cm^{-1}, characteristic of the vibrations of the Mo=O bond of the cis-dioxomolybdenum group [10]. However, the IR-spectroscopic data do not make it possible to judge unambiguously the conformation of the ligand molecule and, consequently, the position of localization of the coordination bond in the complex.

The molecular structure of (II) and the principal geometric parameters are given in Fig. 3. In the investigated complex the molybdenum atom is coordinated at the vertices of an octahedron. The dioxo group of $\mathrm{MoO_2}^{2+}$ has the cis structure typical of the complexes of d^0 metals of groups V-VII in the higher degrees of oxidation [10]. The N(1) atom of the benzothiazole ring and the N(3) atom of the pyrazole ring of the bidentate ligand L occupy the trans positions to the oxo oxygen atoms. The chlorine atoms in the trans positions to each other (and cis to $\mathrm{O_{oxo}}$) make up the coordination polyhedron of the Mo atom. The five-membered metallocycle $\mathrm{MoN_3C}$ has the envelope conformation. [The molybdenum atom is deflected from the plane of the N(1-3) and C(1) atoms by 0.132 Å.]

The Mo—O (oxo) distances in the structure (II) [1.680 and 1.690(5) Å] correspond to a multiple bond and lie in the range of Mo=O values (1.66-1.77 Å) in 34 monomeric octahedral dioxo complexes of molybdenum(VI) with oxygen or nitrogen atoms at the trans positions to the multiply bonded oxo ligand [11,12].*

As usual, the Mo—N bonds, trans in relation to Mo=O, are appreciably elongated as a result of the trans effect of the multiply bonded oxo ligands. The average Mo—N(L) distance (2.310(5) ± 0.013 Å) lies at the lower end of the range of values for the lengths of the analogous Mo—N(A) bonds in 12 structures (2.308—2.486 Å [11]). The average value for the length of the Mo—Cl bond (2.357(2) ± 0.004 Å), cis in relation to Mo=O, is also comparable with published data ($\mathrm{Mo{-}Cl_{cis}}$ = 2.341-2.400 Å in 11 structures [11]).

On account of the absence of like ligands simultaneously in the trans and cis positions to the oxo ligands in the structure of (II) we cannot assess the magnitude of the structural manifestation of the trans effect of the Mo=O multiple bond directly in the form of the difference $\Delta_{\mathrm{trans-cis}}$. It can only be stated that the Mo—N distances, trans in relation to Mo=O, in the structure of (II) are increased by an average of 0.19 Å compared with the standard ("expected") length of the $\mathrm{Mo{-}NR_3}$ bond (2.12 Å [13]) and are on the average 0.10-0.19 Å larger than the Mo—N(A) distance in the cis position to the Mo=O bonds in the three monooxo complexes of Mo(V) known from the literature: $\mathrm{(C_9H_7NO)[MoOCl_3(ONC_9H_6)]}$ (2.198 Å [14]); [MoO(Salen)(MeOH)]Br (2.119 Å [15]) and $\mathrm{MoOCl(NSC_6H_6)_2}$ (2.210 Å [16]).

The angular distortions in the coordination polyhedron of the metal in the structure of (II) are also typical of this type of compound. The O(oxo)MoO(oxo) angle is greatly increased [to 105.1(2)°] and lies in the range of values of 101.0-109.9° in 32 $\mathrm{MoO_2}^{2+}$ structures [11,12], while the opposite chelate angle NMoN is greatly reduced against the ideal value of 90° [to 68.9(2)°]. On the whole the O(oxo)MoO(oxo) angles are always the largest, while the opposite angles involving the atoms in the trans positions to O(oxo) are the smallest in the structure.

As in other $\mathrm{MoO_2}$ complexes, the Mo—Cl bonds, cis in relation to Mo=O, are turned from the Mo=O bonds as a result of coulombic repulsion of the electron clouds of the multiply bonded ligands situated in the cis positions, and this leads to strong bending of the opposite $\mathrm{Mo{-}Cl_{cis}}$ bonds. The ClMoCl angle in (II) [159.15(8)°] lies in the range of

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*A full résumé of the geometric parameters for the monomeric octahedral dioxo complexes of Mo(VI) with n-dentate ligand A (n = 2-4) and Mo—N(A) bonds trans in relation to Mo=O was given in [11], and data for the analogous complexes with O(mono) atoms and bidentate ligands trans in relation to O(oxo) were given in [12].

values for the Cl—Mo—Cl(cis) angles according to the published data (155.5-165.9°). The O(oxo)—Mo—N(Cl) angles are larger than 90° [90.4-96.0(2)°], while the NMoCl angles are less than 90° [79.9-83.1(1)°]. The opposite Mo=O and Mo—N bonds are substantially nonlinear [$OMoN_{trans}$ angles 159.1 and 164.5(2)°]. As usual the Mo atom is displaced from the center of the octahedron toward the multiply bonded oxo atoms [to the O(1)—O(2) edge] by 0.220 Å.

The Conformation of the Ligand Molecule in the Complex. With the similarity of the structure of the ligand molecule in structures (I) and (II) (see Figs. 1 and 3) it is necessary to note the substantial difference in its conformations in the free state and as ligand in the MoO_2Cl_2·L complex, concerning the mutual arrangement of the benzothiazole and pyrazole rings. During complex formation the pyrazole ring is turned by ~180° about the C(1)—N(2) bond in relation to the benzothiazole ring: Torsion angles S(1)—C(1)—N(2)—C(10) = —164.4° in (I) and 1.1° in (II); N(1)—C(1)—N(2)—N(3) = —170.4° in (I) and 3.4° in (II). The mutual arrangement of the ligand molecule in structures (I) and (II) is shown in Fig. 4.

Such a change in the conformation is explained, on the one hand, by the tendency of the sulfur atom to form attracting secondary bonds and, on the other, by the preference for molybdenum to coordinate through the nitrogen atom compared with the sulfur atom (with competition between the donor centers in the polydentate ligand). In the complex (II), as a result of the rotation of the pyrazole ring about the C(1)—N(2) bond and the approach of the N(1) and N(3) atoms (N(1)···N(3) = 2.612 Å) during closure of the metal ring Mo—N(1)—C(1)—N(2)—N(3) the secondary interaction involving the sulfur atom acquires substantially different character. In structure (II) we are concerned with a rare case of shortened intramolecular S···C contacts (S···C(10) 3.315 and S···C(12) 3.123 Å with the sum of the van der Waals radii of S and C equal to 3.55 Å [4]). In particular, the short contact between the sulfur atom and the hydrogen atom of the methyl group, which makes up the T-shaped configuration of the bonds about the S, is not quite typical [S···H(123) 2.74 Å, angles C(2)S(1)H(123) 161, C(2)S(1)C(12) 163.6, S(1)H(123)C(12) 113°). It should be noted that such unusual shortened S···C contacts are due to steric reasons, i.e., the sufficient rigidity of the molecule of L chelated by the Mo atom and, in particular, the impossibility of deflection of the methyl atom C(12) from the S atom. [The C(12) atom is equally distant from the N(2) and C(9) atoms at 2.551 and 2.580 Å respectively.] In addition, the sulfur atom forms a short intermolecular S···O(2) contact of 2.976 Å with the oxo atom of the complex due to the initial symmetric transformation x—½, ½—y, ½+z.

The only consequence of the closure of the chelate ring is a decrease in the cyclic angle N(1)C(1)N(2) to 118.1(6)° in the complex (II) [in the free molecule of (I) the N(1)C(1)N(2) angle is 125(1)°], while the secondary S(1)···N(3) interaction in structure (I) leads to a decrease of the S(1)C(1)N(2) angle and to a lesser degree the C(1)N(2)N(3) angle [118(1) and 114(1)° respectively in (I); 123.8(5) and 116.0(5)° in (II)]. Another consequence of the coordination of the molecule L with the metal is some extension of the N(1)—C(3) and N(3)—C(8) bonds with the participation of the donating nitrogen atoms in the structure of the complex (II) compared with (I) [N(1)—C(3) 1.414(10) and 1.34(2), N(3)—C(8) 1.330(10) and 1.29(2) Å in (II) and (I) respectively].

The free molecule of the ligand in the structure (I) is substantially less planar than the ligand in the complex (II); the departures from the average plane for the individual atoms amount to +0.19 Å [for C(10)] and —0.20 Å [for N(3)], whereas the maximum deviation from the average plane in structure (II) amounts to 0.101 Å for the S(1) atom. (The Mo atom deviates from the average plane of the ligand L by only —0.106 Å.) The dihedral angles between the planar [±0.002—0.015 Å in (II); 0.01-0.05 Å in (I)] rings N_2C_3, NSC_3, and C6 and the N(1), C(1), N(2), N(3) fragment lie in the range of 1-4 and 3-14° in structures (II) and (I) respectively.

The Stacking of the Structural Units in the Crystals of (I) and (II). There are no short intermolecular contacts less than the sum of the van der Waals radii of the respective atoms* in the structure of (I) except for the contacts C(4)···H(111) 2.65 Å and H(113)—H(123) 2.18 Å (to the complexes due to the initial symmetrical transformations x—½, 1—y, ½—z and x, ½+y, ½—z respectively). The other shortest intermolecular contacts in the structure of (I) are: S···C 3.742, N···H 2.80 Å.

In the structure of (II), apart from the above-mentioned S(1)···O(2) contact of 2.976 Å, there are five other contacts less than the sum of the van der Waals radii: Cl(1)···H(121) 2.85 Å (to the complex, ½—x, ½+y, ½—z), O(1)—H(123) 2.50 and O(2)—H(7) 2.58 Å (to the complex ½+x, ½—y, z—½), H(5)—H(111) 2.12 and H(6)—H(9) 2.38 Å (to the complex x, 1+y, z). The other shortest intermolecular contacts in the structure of (II) are as follows: S···C 3.704, Cl···Cl 3.651, C···C 3.468, C···H 2.96 Å.

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*Van der Waals radii (according to Pauling [8]): H 1.2; O 1.4; N 1.5; C 1.7; Cl 1.8; S 1.85 Å.

Each molecule of (I) is in contact with 12 neighboring molecules at distances r_{ij} not exceeding the sum of the van der Waals radii of the respective atoms by more than 0.2 Å ($\Delta_{ij} \leq 0.2$ Å). The molecular coordination number is also equal to 12 for the molecule of the complex (II) ($\Delta_{ij} < 0.2$ Å).

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