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A NEW TYPE OF BENZOTRIAZOLE COORDINATION IN CARBONYL COMPLEXES OF MOLYBDENUM

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Summary

We report the synthesis of new complexes of molybdenum carbonyl with benzotriazole and 1-methylbenzotriazole in which heterocycles containing the NH or NCH_3 group still act as bidentate ligands.

Crystals of the benzotriazole derivative were subjected to an X-ray study. Its structure is built of complex molecules $(BtH)_3Mo_2(CO)_6$ linked with THF molecules via hydrogen bonds. The molecule has the crystallographic symmetry C_s with the Mo atoms, two CO groups and one benzotriazole ligand in the symmetry plane.

Introduction

Benzotriazole (BtH) and its derivatives have been attracting investigators attention for a long time because of the various aspects of their industrial application (corrosion inhibitors, cover stabilizers etc.). In particular, there is much information in literature concerning the coordination properties of benzotriazole (and its anion) as ligands in complexes with metals [1–5]. Both benzotriazole itself and its anion are capable of acting as monodentate ligands with a σ-bond. Ionic derivatives of cyclopentadienyldicarbonyliron $[C_5H_5Fe(CO)_2C_6H_4N_3H]^+$ A^- with $A^- = HSO_4^-$ or $H_2PO_4^-$ and neutral cyclopentadienyl complexes of molybdenum, e.g. $C_5H_5Mo(CO)_2(C_6H_4N_3H)Cl$ [2] have been isolated and studied. The benzotriazole anion (Bt^-) can act as a mono- or bidentate σ-bonding ligand. Neutral derivatives of cyclopentadienyldicarbonyliron e.g. $C_5H_5Fe(CO)_2C_6H_4N_3$, wherein the nitrogen atom of the benzotriazole residue occupies one site of the coordination sphere are known [3]. A large number of binuclear complexes of various metals (Ni, Cu) has been obtained in which benzotriazole residues act as bridging bidentate ligands [4,5]. However, up to now, there were no communications concerning realization of π-bonding and bidentate σ-bonding of benzotriazoles with NH protons. There was no corresponding information on other S and Group V triazoles.

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TABLE 1

ATOMIC COORDINATES ($\times 10^3$, for Mo $\times 10^4$) AND THERMAL FACTORS B_j (Å^2)

Atom	x	y	z	$B_j(\times 10)$	Atom	x	y	z	$B_j(\times 10)$
Mo(1)	0	0	6317(2)	[b]	Solvent molecules of THF [b]				
Mo(2)	440(3)	0	8836(2)	[a]	*Molecule 1*				
O(1)	251(4)	0	514(2)	62(8)	O(T1)	−403(3)	0	516(2)	5(1)
O(2)	−105(2)	−123(1)	504(1)	44(4)	C(T11)	−403(4)	72(2)	47(2)	7(1)
O(3)	−177(4)	0	1014(2)	84(9)	C(T21)	−471(4)	41(2)	382(2)	7(1)
O(4)	−179(2)	116(1)	999(1)	56(5)	*Molecule 2*				
N(1)	−210(3)	0	778(2)	32(7)	O(T2)	107(2)	219(1)	979(1)	6(1)
N(2)	−189(3)	0	711(2)	24(6)	C(T12)	21(6)	284(3)	978(3)	11(1)
N(3)	−316(3)	0	665(1)	26(6)	C(T22)	−51(6)	290(3)	1059(3)	11(1)
N(4)	75(2)	87(1)	720(1)	16(3)	C(T32)	43(4)	272(2)	1116(2)	8(1)
N(5)	58(2)	89(1)	802(1)	24(4)	C(T42)	124(5)	194(2)	1064(2)	18(1)
N(6)	113(2)	151(1)	830(1)	31(4)	*Molecule 3*				
C(1)	148(5)	0	554(2)	39(9)	O(T3)	−329(4)	−206(2)	666(2)	12(1)
C(2)	−64(3)	−75(1)	554(1)	49(7)	C(T13)	−202(6)	−213(3)	716(3)	10(1)
C(3)	104(3)	0	959(1)	61(9)	C(T23)	−158(7)	−301(4)	680(4)	15(2)
C(4)	−141(3)	−77(2)	949(1)	41(6)	C(T33)	−234(6)	−305(3)	611(4)	12(2)
C(5)	−409(4)	0	723(2)	25(8)	C(T43)	−357(6)	−279(3)	605(3)	12(2)

C(6)	−552(5)	0	719(2)	52(9)	*Molecule 4*				
C(7)	−620(5)	0	799(3)	36(9)	O(T4)	440(9)	0	140(7)	16(3)
C(8)	−556(5)	0	872(3)	62(9)	O′(T4)	−361(9)	0	159(7)	14(3)
C(9)	−418(3)	0	886(2)	24(7)	C(T14)	503(7)	−72(3)	158(3)	13(2)
C(10)	−347(4)	0	806(2)	36(9)	C(T24)	617(8)	−51(5)	156(5)	7(2)
C(11)	167(3)	199(2)	770(2)	34(6)	C′(T24)	363(9)	−34(5)	184(5)	8(2)
C(12)	221(5)	268(3)	768(3)	89(9)	*Molecule 5*				
C(13)	276(4)	300(2)	703(2)	58(7)	O(T5)	−105(9)	24(1)	266(5)	3(2)
C(14)	260(3)	256(2)	623(2)	53(7)	C(T15)	102(8)	0	290(5)	11(2)
C(15)	195(3)	179(2)	628(2)	37(5)	C(T25)	−15(9)	0	329(4)	11(2)
C(16)	148(3)	152(1)	701(1)	27(5)	C(T35)	43(7)	67(4)	231(4)	3(2)
					C(T45)	−22(9)	0	193(4)	10(2)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	13(2)	35(2)	19(1)	0	1(1)	0
Mo(2)	16(2)	24(2)	15(1)	0	0	0

[a] Anisotropic thermal factors in the form: $T = \exp[-0.025(B_{11}a^{*2}h^2 + \ldots + 2B_{12}a^*b^*hk + \ldots)]$. [b] Molecules 2 and 3 occupy general positions, 1 and 4 intersected by *m* plane (atoms O(T4) and C(T24) are disordered over two positions with occupancies 0.5), atoms C(T15), C(T25) and C(T45) of molecule 5 lie in the *m* plane, while O(T5) and C(T35) occupy each two positions related by this plane.

The present paper reports the synthesis of new complexes of molybdenum carbonyl with benzotriazole and 1-methylbenzotriazole in which the heterocycles containing the NH or NCH_3 group still act as bidentate ligands.

Results and discussion

We have investigated the reaction of tris-acetonitriletricarbonylmolybdenum with benzotriazole and 1-methylbenzotriazole. The reaction was performed in tetrahydrofuran (THF) medium at room temperature and resulted in stable dark-red crystalline compounds. Crystals of the benzotriazole derivative were subjected to an X-ray study. Its structure is built up of complex molecules $(BtH)_3Mo_2(CO)_6$ (I) linked with THF molecules via hydrogen bonds. Crystals are orthorhombic, at -120°C $a = 10.006(3)$, $b = 17.312(6)$, $c = 16.140(9)$ Å, $Z = 2$, space group $P2_1mn$. Atomic coordinates and temperature factors are listed in Table 1. The binuclear molecule, shown in Fig. 1 with mean values of equivalent bond lengths and angles, has the crystallographic symmetry C_s with Mo atoms, two CO groups and one benzotriazole ligand in the symmetry plane. In the molecule both $Mo(CO)_3$ fragments are bonded to the N atoms of three bridging benzotriazole ligands. The Mo atoms have a distorted octahedral coordination (Table 2) with three N atoms and three CO groups (average

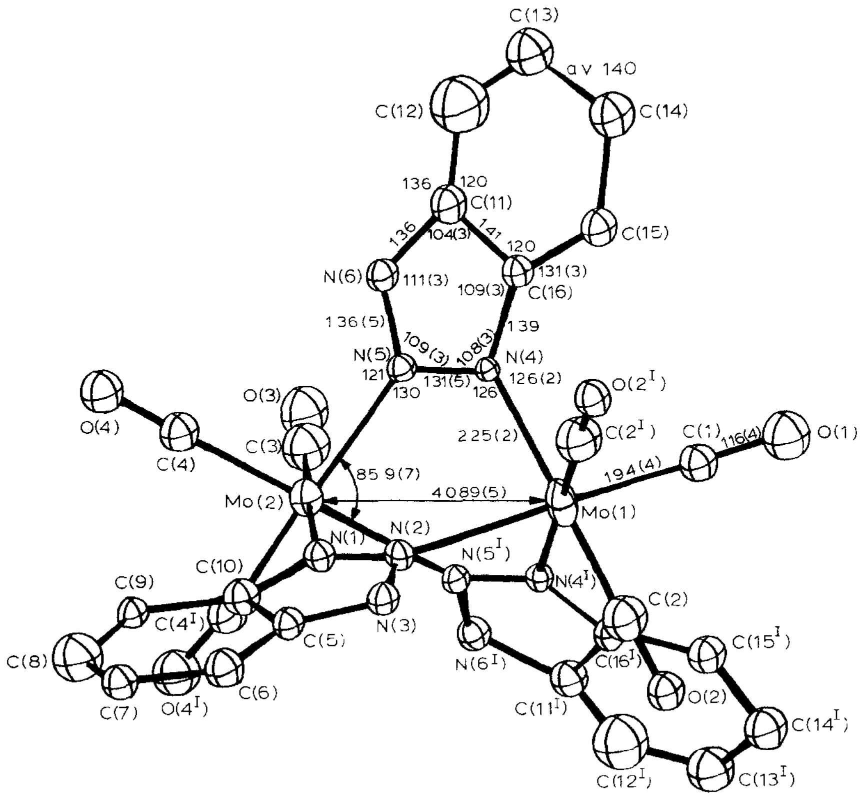

Fig. 1. Molecular structure of $(BtH)_3Mo_2(CO)_6$ E.s.d.: C–C–C angles 3°, Mo–N–N angles 2°, C–C and C–N bond distances 0.05 Å.

TABLE 2

ANGLES ω (deg.) CHARACTERIZING COORDINATION POLYHEDRA OF THE Mo ATOMS IN $L_3Mo_2(CO)_6$

Angles	ω	Angles	ω
N(2)Mo(1)C(1)	174(1)	N(1)Mo(2)C(3)	170(1)
N(2)Mo(1)C(2)	95(1)	N(1)Mo(2)C(4)	89(1)
N(2)Mo(1)N(4)	86(1)	N(1)Mo(2)N(5)	86(1)
C(1)Mo(1)C(2)	80(1)	C(3)Mo(2)C(4)	99(2)
C(1)Mo(1)N(4)	99(1)	C(3)Mo(2)N(5^1)	86(1)
C(2)Mo(1)C(2^1)	85(1)	C(4)Mo(2)C(4^1)	89(1)
C(2)Mo(1)N(4)	179(1)	C(4)Mo(2)N(5)	93(1)
C(2)Mo(1)N(4^1)	94(1)	C(4)Mo(2)N(5^1)	174(1)
N(4)Mo(1)N(4^1)	86(1)	N(5)Mo(2)N(5^1)	85(1)

Mo–CO 1.94(4), average C–O 1.16(4) Å), and each nitrogen atom has one of the CO groups as a *trans* partner. As a result each Mo atom obeys the effective atomic number rule and accordingly, Mo–Mo interaction in the compound is absent (the Mo · · · Mo distance of 4.089(5) Å is considerably greater than the doubled covalent Mo radius 3.16 Å) [6]. The mean value of the Mo–N bond length (2.25(2) Å) is close to those found in other Mo complexes with N atoms acting as two-electron donors, viz. in $(Ph_2B(pz)_2(\eta^3\text{-}CH_2C(Me)CH_2)(CO)_2Mo$ [7] and $(bipyMo(CO)_3(SnCl_2Me)Cl$ [8], the mean Mo–N values are 2.23(1) Å. The presence in the compound studied of three bridging ligands each bonded via their two nitrogen atoms with two Mo atoms results in the formation of three six-membered metallocycles Mo(1)N(4)-N(5)Mo(2)N(5^1)N(4^1), Mo(1)N(2)N(1)Mo(2)N(5)N(4) and Mo(1)N(2)N(1)Mo(2)-N(5^1)N(4^1) with a distinct boat conformation (Table 3 lists the values of torsion angles characterizing the conformation of metallocycles) with the Mo(1) and Mo(2) atoms displaced from the plane N(4)N(5)N(4^1)N(5^1) by 0.92 and 0.85 Å and from the plane N(1)N(2)N(4)N(5) by 0.83 and 0.94 Å, respectively. In the six-membered metallocycle MoN_4 in the structure of $(Ph_2B(pz)_2)(\eta^3\text{-}CH_2C(Me)CH_2)(CO)_2Mo$ [7] the distance of the Mo atom from the plane of four nitrogen atoms is 1.12 Å. In the binuclear allylpalladium complex $(\eta^3\text{-}CH_2CHCH_2)Pd(N_2C_3HMe_2)_2$ [9], with two dimethylimidazole ligands N-coordinated to Pd atoms, the latter are situated at distances of 1.113 and 1.064 Å from the boat bottom, formed by four nitrogen atoms. The stereochemistry of I is characterized by the non-equivalence of the Mo atoms, viz. if the Mo(1) atom is coordinated by one central (N(2)) and two side

TABLE 3

TORSION ANGLES τ (deg.) CHARACTERIZING CONFORMATION OF METALLOCYCLES MoN_4Mo

Angles	τ	Angles	τ
Mo(1)N(2)N(1)Mo(2)	0(2)	N(5)N(4)Mo(1)N(2)	39(2)
N(2)N(1)Mo(2)N(5)	43(2)	N(4)Mo(1)N(2)N(1)	−43(3)
N(1)Mo(2)N(5)N(4)	−46(2)	N(2)N(1)Mo(2)N(5)	−43(3)
Mo(2)N(5)N(4)Mo(1)	3(2)	N(1)Mo(2)N(5^1)N(4)	46(1)

TABLE 4

IR SPECTRA OF THE COMPLEXES

Compound	Solvent	ν(C=O) (cm^{-1})	ν(N–H) (cm^{-1})
I	THF	1820,1913,1925,1928,2030	3560
II	THF	1765,1890	–
III	MeCN	1818,1917	–

(N(4) and N(4^1) atoms of benzotriazole ligands, then the Mo(2) atom, on the contrary, is coordinated by two central (N(5) and N(5^1)) and one side (N(1)) ones, i.e. the molecule I has no non-crystallographic three-fold axis. The geometric parameters of the planar benzotriazole ligands are close to those found in other non-coordinated derivatives of benzotriazole [10]. The dihedral angles between the mean planes of these ligands are 117, 117 and 126°. The structure of I also contains solvating THF molecules, two of which participate in formation of hydrogen bonds with the NH protons of benzotriazole ligands: OT(1) ··· N(3) 2.56 Å, OT(2) ··· N(6) 2.68 Å, OT(1)N(3)N(1) 140°, OT(1)N(3)C(5) 116°, OT(2)N(6)N(5) 132° and OT(2)N(6)C(11) 112°. Thus, two out of three NH protons of the BtH ligands in I participate in formation of hydrogen bonds. The THF molecules OT(4) and OT(5) are disordered and high temperature factors of the THF OT(3) atoms do not exclude its probable disordering. Disorder of the structure seems to result in the moderate accuracy of determination of geometrical parameters.

The IR spectra of complex I obtained in THF solution are in good agreement with the data of the X-ray structural analysis (see Table 4). There are five absorption bands in the region from 1850–2050 cm^{-1} characteristic of carbonyl ligands. This spectrum also has a broad band centered at 3560 cm^{-1} which we ascribe to the stretching vibrations of the hydrogen bond.

The PMR spectrum of complex I obtained in THF solution yields a characteristic ABXY proton multiplet of the BtH benzogroup with the centre at ca. 7.65 ppm. NH protons are observed as a broad singlet at ca. 15.4 ppm.

The presence of NH protons in complex I is confirmed by its reaction with sodium hydride. The reaction is accompanied by hydrogen evolution and produces a yellow-greenish compound which changes its colour into a reddish when exposed to air. The elemental analysis corresponds to the formula $(C_6H_4N_3Na)_3Mo_2(CO)_6 \cdot x$ 2.5THF (II). The IR spectrum of II in acetonitrile contains two broad unresolved bands in the frequency region of terminal CO groups (Table 4).

The 2,3 coordination of BtH with molybdenum tricarbonyl groups affords, in

TABLE 5

PMR SPECTRA OF THE COMPLEXES

Compound	Solvent	Protons of benzo group (ppm)	δ(N–H) (ppm)
I	THF	7.65	15.4
II	THF	7.34	–
III	MeCN	7.45	–

principle, the possibility of formation of complexes with 1-substituted benzotriazoles. We have obtained a complex with 1-methylbenzotriazole (III). Its spectral characteristics are listed in Tables 4 and 5. As expected III does not react with sodium hydride.

Experimental

All syntheses and preparation of samples for spectral investigations were performed under argon. Tris-acetonitrilemolybden tricarbonyl was obtained according to the techniques previously described [11]. Benzotriazole was purified by distillation under vacuum. 1-Methylbenzotriazole was obtained by the action of methyl iodide on an alkaline BtH solution in alcohol with subsequent separation of the isomers and distillation in vacuo.

PMR spectra were obtained with a R-20 instrument. The IR spectra were registered with an UR-10 spectrometer.

An X-ray structural investigation of complex I was carried out with a Syntex-P2_1 diffractometer (λ-Mo-K_α, graphite monochromater, measurement at -120°C, 1890 reflections with $F^2 \geqslant 2\sigma$). The structure was solved by the heavy atom method and refined by the least squares method in anisotropic(Mo)-isotropic approximation to $R = 0.107$ ($R_w = 0.113$).

Reaction of (MeCN)$_3$Mo(CO)$_3$ with BtH

0.4 g of $(MeCN)_3Mo(CO)_3$ and 24 g of BtH were stirred in 70 ml of THF for 1 h. Then the solution was removed under vacuum of a water-jet pump. A small amount of THF (10 ml) was added to the dry residue and the solution was loaded onto a SiO_2 column. The complex was eluted with ester. The obtained dark-red solution was crystallized at a low temperature. Yield 0.45 g (76%).

IR spectrum (THF): 1890s, 1913s, 1925m, 1928m, 2030w cm^{-1}.

Found: C, 45.70; H, 4.12; N, 14.30; Mo, 21.41. Calcd. for $C_{34}H_{35}N_9O_{8.5}Mo$: C, 45.48; H, 3.90; N, 14.05; Mo, 21.40%.

Synthesis of the Na salt of complex I

0.45 g of complex I and 0.036 g of NaH were stirred in THF for 5 h. The suspension was transferred onto a column with a porous filter and eluted with THF until the appearance of a light yellow eluate and the complex then eluted off with hexane. The obtained yellow-green residue was dried under vacuum. Yield 0.3 g (63%).

IR spectrum (MeCN): 1765s, 1890s cm^{-1}

Found: C, 42.72; H, 3.81; N, 13.27. Calcd. for $C_{34}H_{32}Na_3N_9O_{8.5}Mo$: C, 42.38; H, 3.35; N, 13.06%.

Reaction of (MeCN)$_3$Mo(CO)$_3$ with 1-methylbenzotriazole

0.4 g of $(MeCN)_3Mo(CO)_3$ and 0.27 g of 1-methylbenzotriazole were stirred in 70 ml of THF for an hour. The solvent was removed under vacuum of a water-jet pump. 10 ml of THF were added to the dry residue and the solution was loaded onto a SiO_2 column. The complex was eluted with ester. The dark red solution obtained was crystallized at a low temperature. Yield 0.42 g (74%).

IR spectrum (THF): 1818s, 1917s cm^{-1}
Found: C, 46.18; H, 3.80; Mo, 22.24. Calcd. for $C_{33}H_{31}N_9O_{7.5}Mo$: C, 45.69; H, 3.81; Mo, 22.15%.

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