



Preparation and use of novel molybdenum-containing organic complexes as catalysts in the epoxidation of cyclohexene

II. Synthesis and applicability of molybdenum complexes based on squaric acid, 1-phenyl-1-ethanamine and 1,3-diamino-2-propanol

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Abstract

Two novel molybdenum-containing organic complexes based on 3,4-dihydroxy-3-cyclobutene-1,2-dione (“squaric acid”), 1-phenyl-1-ethanamine and 1,3-diamino-2-propanol (DAP), respectively, have been synthesized in aqueous medium and characterized by infrared (FT-IR) spectroscopy, thermogravimetric (TGA) and elemental analyses. The catalytic activities and selectivities of these complexes in the epoxidation of cyclohexene with *t*-butylhydroperoxide (TBHP) were, approximately, the same as those of similar complexes prepared previously in the same manner.

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1. Introduction

Molybdenum-containing complexes have long been known as useful catalysts for the epoxidation of alkenes by organic hydroperoxides. The industrial implementation of this reaction was first achieved in the *Halcon* process, which utilized a soluble Mo complex, and in the *Arco* process, which made use of a heterogeneous Ti-SiO₂ catalyst to effect the epoxidation of propylene to the synthetically useful propylene oxide precursor [1,2]. Since then, a number of soluble molybdenum organic complexes with carboxylic acids, ketones, alcohols, glycols, amines, etc. have been synthesized and employed as homogeneous catalysts for the epoxidation of various alkenes [3–7]. An excellent review covering this vast research area has also appeared [8]. It is also worth mentioning the publications on the epoxidation of alkenes in the presence of various molybdenum peroxocomplexes as catalysts, and the discussions concerning both the structural and mechanistic aspects of this important catalytic

reaction [9–12]. The preparation of polymer-supported catalysts for the epoxidation of alkenes has also received scientific attention since the late 1970s. Recently, a number of chelating functional molybdenum-containing copolymers have been prepared and used as catalysts for the epoxidation of alkenes, mostly, cyclohexene [13–15].

Compared to the vast number of organic ligands employed so far for the preparation of molybdenum complexes and catalysts for the alkene epoxidation, 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid) holds specific position. The squarate dianion possesses a square-planar structure (D_{4h} symmetry) and has been suggested as a member of an aromatic series of cyclic oxocarbon anions that are stabilized by delocalization of π -electrons around the ring [16,17]. Therefore, it appears particularly attractive as a template for generating self-assemblies from polarizable cations in general and organic bases in particular. Such complexes are expected to serve as efficient catalysts for various organic reactions.

In our recent work [18], we reported on the synthesis of three novel molybdenum organic complexes by one-pot procedure of interaction of squaric acid, molybdenum

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dioxydichloride and several polyfunctional organic amines [monoethanolamine (MEA), triethanolamine (TEA) and guanidinium carbonate (as a source of guanidine (Gua))], respectively. These complexes were used as homogeneous catalysts for the epoxidation of cyclohexene with *t*-butylhydroperoxide (TBHP) and showed activities and selectivities close to those of the well known commercial molybdenyl acetylacetonate. The aim of the present work was to prepare two more novel molybdenum complexes, containing squarate moiety and other, structurally different, organic amines as ligands by employing similar procedures, and to compare the results concerning their syntheses, characterization and applicability as epoxidation catalysts with those obtained by us previously.

2. Experimental

2.1. Starting material

3,4-Dihydroxy-3-cyclobutene-1,2-dione (squaric acid, H₂Sq, 98%) was obtained from Huls-Marl (Germany) and was recrystallized before use. *S*-(-)-1-Phenyl-1-ethanamine (PhEA) (Fluka AG), 1,3-diamino-2-propanol (DAP) (Riedel de Haen) and molybdenum (VI) dioxodichloride (molybdenyl chloride, MoO₂Cl₂, Aldrich) were employed without further purification. Cyclohexene (Merck-Schuchardt, 99%) and *t*-butylhydroperoxide (Fluka AG) were also used as received.

2.2. Syntheses of the molybdenum-containing complexes

2.2.1. Synthesis of the complex **D**

2.2.1.1. Preparation of 1-phenyl-1-ethanamonium squarate (H₂Sq·2PhEA). 0.342 g (3 mmol) squaric acid (H₂Sq) was placed into a small 50 ml beaker and then 6 ml distilled water were added. The suspension was slowly heated, with stirring, to 60–80 °C until the squaric acid was completely dissolved. Then 0.727 g (6 mmol) *S*-(-)-1-phenyl-1-ethanamine, dissolved in 3 ml 96% ethanol were gradually added to the hot solution and the stirring was continued for 0.5 h at room temperature. Slow evaporation for several days produced colorless needles, which were thoroughly filtered under vacuum and left to dry out in air for 24 h. Yield: 0.702 g. Anal. Calc. for C₂₀H₂₄N₂O₄: C, 67.41; H, 6.74; N, 7.86. Found: C, 67.31; H, 6.55; N, 7.88.

The following infrared absorptions were obtained in the 4000–400 cm⁻¹ region (mid IR spectra, KBr pellets, cm⁻¹): 3029 (sh), 3007 (sh), 2971 (m), 2931 (m), 2857 (m), 2766 (m), 2718 (m), 2684 (m), 2629 (m), 2544 (w), 1631 (m), 1607 (w), 1531 (m), 1497 (vs), 1475 (vs), 1443 (vs), 1381 (m), 1375 (m), 1316 (w), 1293 (w), 1236 (w), 1187 (w), 1161 (w), 1094 (m), 1083 (m), 1070 (m), 1030 (w), 1014 (w), 1002 (w), 983 (w), 920 (w), 888 (vw), 849 (vw), 780 (w), 770 (m), 763 (m), 700 (m), 620 (w), 558 (w), 481 (w).

2.2.1.2. Synthesis of the molybdenum-containing complex (complex **D).** 0.233 g (2.04 mmol) H₂Sq were placed into a small 50 ml beaker and 10 ml distilled water were added. The suspension was slowly heated, with stirring, between 60–80 °C until the squaric acid was completely dissolved. 0.489 g (4.04 mmol) PhEA, dissolved in 3 ml 96% ethanol were added to the hot solution and the stirring was continued for 0.5 h at room temperature. This was followed by a gradual addition of 0.800 g (ca. 4 mmol) MoO₂Cl₂, which produced a green suspension. The stirring was continued for another 0.5 h at room temperature. Then, the suspension was filtered under vacuum and washed thoroughly with 70–80 ml distilled water, which resulted in its dissolution and almost no solid residue remained on the filter. The light green solution was left to evaporate slowly, the solid obtained was dissolved in 20 ml acetone and the mixture was subjected to a second evaporation at room temperature. The final solid obtained was filtered under vacuum, washed with ether and dried at room temperature in air. Yield: 0.260 g. Anal. Calc. for C₂₀H₂₈N₂Mo₃O₁₅: C, 29.13; H, 3.40; N, 3.40; Mo, 34.95. Found: C, 29.47; H, 2.85; N, 3.64; Mo, 36.00. IR: 3033 (m), 2979 (m), 2927 (m), 1806 (w), 1633 (s), 1544 (s), 1507 (vs), 1477 (vs), 1387 (w), 1315 (w), 1291–1100 (w), 1090 (m), 1062 (w), 1029 (w), 942 (s), 907 (vs), 798–699 (m), 669 (s), 599 (s), 539–509 (w).

2.2.2. Synthesis of the complex **E**

2.2.2.1. Preparation of 2-propanol-1,3-diamonium squarate (H₂Sq·DAP). 0.458 g (4.02 mmol) H₂Sq were placed into a small 50 ml beaker and 20 ml distilled water were added. The suspension was slowly heated, with stirring, to 60–80 °C until the squaric acid was completely dissolved. 0.363 g (4.03 mmol) 1,3-diamino-2-propanol (DAP) were then added to the hot solution and the stirring was continued for 1 h at room temperature. Slow evaporation for several days produced colorless to white crystalline product which was filtered under vacuum and left to dry out in air for 24 h. Yield: 0. Anal. Calc. for C₇H₁₂N₂O₅: C, 41.18; H, 5.88; N, 13.73. Found: C, 40.87; H, 5.64; N, 14.46. IR: 3189–2591 (m), 1640 (m), 1604 (m), 1544 (s), 1526 (s), 1492 (vs), 1452 (m), 1436 (m), 1357 (m), 1313 (m), 1193 (m), 1139 (w), 1088 (m), 1055 (m), 1015 (m), 980 (m), 869 (w), 816 (w), 717 (w), 655 (w), 642 (w), 548 (w), 499 (w), 427 (w).

2.2.2.2. Synthesis of the molybdenum-containing complex (complex **E).** 0.458 g (4.02 mmol) H₂Sq were placed into a small 50 ml beaker and then 10 ml distilled water were added. The suspension was slowly heated, with stirring, to between 60 and 70 °C until the squaric acid was completely dissolved. 0.363 g (4.03 mmol) DAP were then added to the hot solution, followed by 0.800 g (ca. 4 mmol) MoO₂Cl₂ which produced almost immediately green suspension. The stirring was continued for 2 h. The resulting suspension was filtered under vacuum, washed consecutively and thoroughly with distilled water, acetone and ether and dried

at room temperature in air. Yield: 0.856 g. Anal. Calc. for $C_7H_{16}N_2Mo_3O_{16}$: C, 12.50; H, 2.38; N, 4.17; Mo, 42.86. Found: C, 11.82; H, 1.29; N, 3.69; Mo, 43.30. IR: 3250–3000 (wide massive; no pronounced bands observed), 1806 (w), 1631 (m), 1555 (vs), 1521 (vs), 1478 (s), 1343 (w), 1228 (w), 1180 (w), 1114 (w), 1092 (w), 1006 (w), 940 (s), 915 (sh), 897 (s), 796 (w), 713 (m), 670 (sh), 600 (sh), 544 (vs), 422 (w).

2.3. Catalytic epoxidations

For a typical experimental procedure, an amount of the catalyst, equivalent to 0.033 mmol Mo and 6.6 ml (0.065 mol) cyclohexene were placed into a three-necked 12 cm³ thermostated glass reactor fitted with a reflux condenser, thermometer and a septum cap. The mixture was stirred for 5 min at 79 °C and then 1 ml (ca. 0.010 mol) anhydrous *t*-butylhydroperoxide was added. No solvent was used in the epoxidation reaction; an excess of cyclohexene reactant was placed in the reaction mixture instead. The reaction was monitored at certain time intervals to determine the concentrations of TBHP and 1,2-epoxycyclohexane (cyclohexene oxide) and was left to proceed until near complete conversion of the TBHP. At this point, a sample for the GLC determination of the reaction products was collected.

2.4. Instrumentation and analyses

Gas–liquid chromatographic (GLC) analyses of the products obtained from the epoxidation reaction were performed on a SIGMA 2000 instrument (Perkin-Elmer, Norwalk, CT, USA) equipped with a flame ionization detector. Data handling was provided by Chromatographics 2 Data System (Perkin-Elmer). The chromatograph was fitted with Permaphase DMS (polydimethylsiloxane) fused-silica capillary column (50 m × 0.25 mm). The oven temperature was 70 °C and nitrogen (30 psi) was the carrier gas. GLC analysis was combined with both the titrimetric determination of alkene oxide in non-aqueous medium [19] and standard hydroperoxide iodometric method. The molybdenum content in the complexes synthesized was evaluated by thermal gravimetric analysis (TGA) using an OD-102 instrument (MOM, Hungary) by burning the sample to MoO₃ at 650–700 °C with the complete loss of organic matter [20]. The IR spectrum of the inorganic residue was identical to that of commercial MoO₃. The results from the TGA were found to correspond to those obtained from the colorimetric method for molybdenum analysis, based on the formation of colored complexes with thiocyanate [21]. Generally, the thermal analyses (TGA/DTA) were conducted on the same instrument at a heating rate of 10 °C/min over the temperature range 20–750 °C in air. The elemental microanalyses were performed on the Carlo Erba instrument (Italy). The FT-IR spectra of the samples were run on Bruker IFS-113 spectrometer as KBr pellets in the 4000–400 cm⁻¹ regions.

3. Results and discussion

3.1. Preparation and characterization of the squaric acid salts and molybdenum-containing complexes


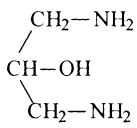
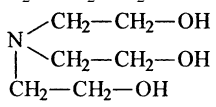
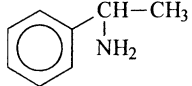
In the course of our previous studies [18], it was found that introducing H₂Sq, the organic amine and MoO₂Cl₂ consecutively into the reaction in one single step (one-pot procedure) favored the formation of the corresponding complexes. However, the preparation of the squaric acid salts with the organic bases was also conducted separately in order to prove their formation and to compare their spectral characteristics with those of the corresponding molybdenum complexes.

The salts of H₂Sq with the organic bases were found to be crystalline compounds. No melting phenomena were, however, detected. The molybdenum-containing complexes **D** and **E**, on the other hand, did not have pronounced crystalline structures. This, again, prevented us from obtaining samples for X-ray diffraction analysis in order to conduct their full structural characterization, as mentioned also in our previous publication [18]. Moreover, the molybdenum complex **D** was found to be nearly soluble in both the water and acetone, in contrast to the insolubility of complex **E** and complexes **A–C** prepared and studied previously [18]. This was probably due to the monofunctional nature of *S*-(-)-1-phenyl-1-ethanamine employed, which, therefore, did not act as a multidentate ligand in the complex **D** formation.

Due to the generally unknown stoichiometry of their formation, the “yields” of the molybdenum-containing complexes were, approximately, calculated on the mass basis, i.e., the amount of the product was related to the sum of the amounts of reactants (H₂Sq, organic amine and MoO₂Cl₂) introduced. The comparison of the yields of the newly prepared complexes **D** and **E** with those (**A–C**) studied by us previously [18] showed some dependence on the type of organic amine used for their synthesis (Table 1). For example, guanidine, as the strongest organic base employed, acted as multidentate ligand of highly-symmetrical structure and the corresponding complex **C** [18] was obtained with the highest yield. On the other hand, the use of 1,3-diamino-2-propanol (for the preparation of complex **E**), MEA (complex **A** [18]) and TEA (complex **B** [18]) was associated with gradual reduction in the yields of the corresponding molybdenum complexes as the basicity of these amines decreased. Again, the structurally more symmetrical DAP as multifunctional amine and ligand took precedence in terms of the yield of the complex formed. As for *S*-(-)-1-phenyl-1-ethanamine of unknown basicity, the lowest yield of the complex **D** could be explained by the fact that the only functional (amino) group present was completely engaged in the formation of the squarate salt. This made the interaction with MoO₂Cl₂ and Mo coordination difficult indeed.

The FT-IR spectra of the organic salts and the corresponding molybdenum-containing complexes **D** and **E**,

Table 1
Effect of the structure of amines used as ligands on the yield of the molybdenum-squarate complexes

Molybdenum-squarate complex	Structure of the organic amine involved	Conjugate acid pK _a	Yield of the complex (%)
C^a		13.6	53.6
E^b		9.7	52.8
A^a	H ₂ N-CH ₂ -CH ₂ -OH	9.5	50.7
B^a		7.9	44.5
D^b		No data	17.1

^a Complexes prepared previously [18].

^b Newly prepared complexes.

prepared in aqueous solution showed the characteristic fundamental vibrations near 1530 and 1090 cm⁻¹ (Tables 2 and 3). These vibrations have been established for the squarate anion (SQ²⁻) of high (D_{4h}) symmetry in the IR spectra of potassium, sodium and lithium squarates [22,23]. For example, complexes in which the squarate is coordinated through all four oxygen atoms exhibit a strong band near 1500 cm⁻¹, assigned to a mixture of C–C and C–O stretching vibrations [24]. The elemental analysis proved the stoichiometry in the formation of the organic salts. The quantitative determination of nitrogen showed that the amines as additional ligands were definitely present in the structures of the molybdenum complexes. The latter did not

contain chlorine, as proved by the Schoeniger method and the TG analyses showed high molybdenum content.

3.1.1. H₂Sq·2PhEA and complex **D**

The corresponding wavenumbers (cm⁻¹) of the observed characteristic bands in the IR spectra and their assignments [25] for H₂Sq·2PhEA and complex **D** are listed in Table 2.

The series of bands at 2766, 2718, 2684, 2629 and 2544 cm⁻¹ and the lack of pronounced absorptions within 3500–3100 cm⁻¹ are typical for the ammonium (–NH₃⁺-type) salts such as H₂Sq·2PhEA (Table 2). No bands at 1790–1820 cm⁻¹, usually assigned to the localized C=O bonds (free non-coordinated carbonyl) in the squaric

Table 2
Selected vibrational data (cm⁻¹) and their assignment for H₂Sq·2PhEA and complex **D**

H ₂ Sq·2PhEA		Complex D	
Wavenumbers	Assignment	Wavenumbers	Assignment
3029–3007	ν(Ar–H), ν(NH ₃) ⁺	3033	ν(Ar–H), ν(NH ₃) ⁺
2971, 2931–2857	ν(CH ₃)	2979, 2927	ν(CH ₃)
2766–2544	ν(NH) ⁺ , associated, salt “bridges”, NH ⁺ ··· O ⁻ , etc.	–	–
1631, 1607	δ(NH ₃) ⁺ ; vibrational motions for the salt (benzene ring, type 8a and 8b [25,26])	1633	δ(NH ₃) ⁺ ; vibrational motions for the salt (benzene ring, type 8a and 8b [25,26])
1531	ν(C–O) + ν(C–C) (SQ ²⁻)	1544, 1507	ν(C–O) + ν(C–C) (SQ ²⁻)
1497, 1475, 1443	ν(C=C) for benzene ring (19a, 19b and 14 type vibrations)	1477, 1387–1290	ν(C=C) for benzene ring (19a, 19b and 14 type vibrations)
1381–1316	δ(CH ₃) + δ(C–H) (C ₆ H ₅ CH(CH ₃) moiety), δ(C–H) (type 3 vibrations) for benzene ring [25,26]	1387–1290	δ(CH ₃) + δ(C–H) (C ₆ H ₅ CH(CH ₃) moiety), δ(C–H) (type 3 vibrations) for benzene ring
1293, 1236	ν(C ₆ H ₅ –CH–)	1291–1233	ν(C ₆ H ₅ –CH–)
1187–1152	δ(C–H) for benzene ring; ρ(NH ₃) ⁺ , planar	1161	δ(C–H) for benzene ring; ρ(NH ₃) ⁺ , planar
1094–1071	SQ ²⁻ , ν(C–N)	1090–1062	SQ ²⁻ , ν(C–N)
983–780	γ(C–H) for benzene ring	942, 907	cis-MoO ₂ (ν(Mo–O _l))
700	Type 4 vibrations for monosubstituted benzene ring [25,26]	699	Type 4 vibrations for monosubstituted benzene ring [25,26]
650–400	Non-identified	599, 539 (sh), 509 (sh)	Mo–O bonds with O-containing organic ligand (H ₂ Sq)

Table 3
Selected vibrational data (cm^{-1}) and their assignment for $\text{H}_2\text{Sq}\cdot\text{DAP}$ and complex **E**

$\text{H}_2\text{Sq}\cdot\text{2PhEA}$		Complex D	
Wavenumbers	Assignment	Wavenumbers	Assignment
3190	$\nu(\text{OH})$, strong H-bonds	3190–3000 (massive)	$\nu(\text{OH})$, strong H-bonds
2996, 2924, 2852	$\nu(\text{CH}_2)^+$, $\nu(\text{CH})$	2927	$\nu(\text{CH}_2) + \nu(\text{CH})$
2776, 2717, 2685, 2591	$\nu(\text{NH})^+$, associated, salt “bridges”, $\text{NH}^+ \dots \text{O}^-$, etc.	–	–
1640, 1604	$\delta(\text{NH}_3)^+$	1633	$(\text{NH}_3)^+$
1541, 1526, 1492	$\nu(\text{C-O}) + \nu(\text{C-C}) (\text{SQ}^{2-})$	1551, 1522	$\nu(\text{C-O}) + \nu(\text{C-C}) (\text{SQ}^{2-})$
1452, 1436	$\delta(\text{CH}_2\text{-N})$, $\delta(\text{CH}_2)$, $\delta(\text{OH})$	1478	$\delta(\text{CH}_2\text{-N})$, $\delta(\text{CH}_2)$, $\delta(\text{OH})$
1357, 1313	$\delta(\text{OH})$, $\omega(\text{CH}_2)$, $\omega(\text{CH-OH})$	1343, 1282	$\delta(\text{OH})$, $\omega(\text{CH}_2)$, $\omega(\text{CH-OH})$
1193, 1157, 1139	$\nu(\text{C-O})$, $\nu(\text{C-N})$	1180, 1114	$\nu(\text{C-O})$, $\nu(\text{C-N})$
1088	SQ^{2-} , $\nu(\text{C-N})$, $\nu(\text{C-O})$, $\rho(\text{NH}_3)^+$	1092	SQ^{2-} , $\nu(\text{C-N})$, $\nu(\text{C-O})$, $\rho(\text{NH}_3)^+$
1055–980	$\nu(\text{C-C})/\rho(\text{NH}_3)^+$	1053–1006	$\nu(\text{C-C})/\rho(\text{NH}_3)^+$
–	–	940, 915 (sh), 897 (sh)	<i>cis</i> - MoO_2 ($\nu(\text{Mo-O}_t)$)
869–642	$\rho(\text{CH}_2)$, $\rho(\text{CH-OH})$	796, 713, 670	$\rho(\text{CH}_2)$, $\rho(\text{CH-OH})$
548–427	C–C–O (skeletal)	544, 600 (sh)	Mo–O bonds with O-containing organic ligand(s)

acid and at $1630\text{--}1690\text{ cm}^{-1}$ ($\nu(\text{C}=\text{C})$ in H_2Sq) [27] were detected. This, together with the fundamental vibrations at $1531\text{--}1497\text{ cm}^{-1}$ also proved the presence of squarate anion (SQ^{2-}) moiety in the organic salt. The sequence of several absorptions between 1443 and 1316 cm^{-1} for the salt resulted from the considerable split of the typical bands for the CH_3 and CH -groups caused by the $\text{C}_6\text{H}_5\text{-CH}(\text{CH}_3)\text{-NH}_3^+$ moiety. The interaction with MoO_2Cl_2 resulted in some essential changes in the spectrum of complex **D** with respect to the one of $\text{H}_2\text{Sq}\cdot\text{2PhEA}$. The bands between 2766 and 2544 cm^{-1} disappeared, which is likely to indicate some involvement of the adjacent salt-forming fragments (e.g., O^- of the squarate anion) in the formation of the molybdenum-containing complex. The fundamental bands for SQ^{2-} at 1531 and 1497 cm^{-1} for the ammonium salt were shifted towards 1544 and 1507 cm^{-1} , respectively, due to the decrease in the typical D_{4h} symmetry for the squarate as a result of its coordination to the oxomolybdenum fragment. The *new* strong bands at 942 and 907 cm^{-1} detected for the molybdenum-containing complex only can be definitely assigned to the *cis*- MoO_2 fragment with terminal (t) oxygens derived from MoO_2Cl_2 ($\nu(\text{Mo}=\text{O}_t)$), as reported in a number of publications [20,27–29]. The *new* strong absorption at 599 cm^{-1} with shoulders at 539 and 509 cm^{-1} can be attributed to the formation of polar Mo–O bonds with organic ligand functional groups [20].

3.1.2. $\text{H}_2\text{Sq}\cdot\text{DAP}$ and complex **E**

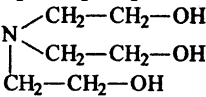

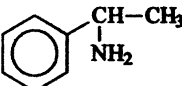
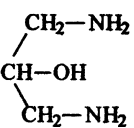
The corresponding wavenumbers (cm^{-1}) of the observed characteristic bands in the IR spectra and their assignments [25] for $\text{H}_2\text{Sq}\cdot\text{DAP}$ and complex **E** are listed in Table 3.

The medium to strong band at 3189 cm^{-1} in the spectrum of $\text{H}_2\text{Sq}\cdot\text{DAP}$ can be assigned to OH-stretching vibrations ($\nu(\text{OH})$) for the DAP fragment with formation of strong hydrogen bonds. The bands at 2776 , 2717 , 2685 , 2591 and 2500 cm^{-1} (sh) are attributed to the two protonated amino groups ($\nu(\text{N-H})$, ammonium ($-\text{NH}_3^+$ -type) salt),

forming also strong hydrogen bonds with SQ^{2-} . The bands at 1640 and 1604 cm^{-1} of medium intensity could be assigned to mixed stretching and bending vibrations of NH_3^+ groups, affected by the interaction with SQ^{2-} ($\nu(\text{NH}_3^+) + \delta(\text{NH}_3^+)$). Again, the fundamental vibrations for SQ^{2-} are represented by the strong and very strong bands observed at 1541 , 1526 and 1492 cm^{-1} . The formation of the molybdenum-containing complex **E** was proved by some significant changes in the corresponding spectrum, compared to that of the ammonium salt. For example, the band at 3189 cm^{-1} ($\nu(\text{OH})$) was replaced by massive of bands around 3120 cm^{-1} and this might be an indication for the engagement of the $-\text{OH}$ group of DAP in the formation of the molybdenum complex. The bands at $2776\text{--}2500\text{ cm}^{-1}$ for the ammonium salt almost disappeared, which, as mentioned above, indirectly proves the formation of the molybdenum-containing complex involving SQ^{2-} . The strongest band observed at 1492 cm^{-1} for the salt was considerably shifted towards 1522 cm^{-1} in the complex and this might be caused by an electronic influence of the MoO_2^{2+} fragment on the fundamental vibration of SQ^{2-} . As stated above, the *new* strong bands at 947 and 915 cm^{-1} (shoulder), detected for the molybdenum-containing complex *only* are assigned to the *cis*- MoO_2 fragment ($\nu(\text{Mo}=\text{O}_t)$). Again, the *new* very strong band at 544 cm^{-1} (shoulder at 600 cm^{-1}) can be attributed to the formation of polar Mo–O bonds with organic ligand functional groups.

In the cases discussed above and concerning complexes **D** and **E** as well as those (**A–C**) prepared previously [18], the characteristic doublets (sometimes with shoulders) observed in both the $900\text{--}950$ and $500\text{--}600\text{ cm}^{-1}$ regions and attributed to the *cis*- MoO_2 fragment and the coordination of MoO_2 towards the organic ligand(s) respectively were of a high analytical value. The positions and the intensities of the corresponding bands depended strongly on the kind of organic amine involved in the complex formation (Table 4). For example, the squarate complexes (**A–C** and **E**) based

Table 4
Characteristic vibrational data (cm^{-1}) associated with the involvement of Mo in the formation of the squaric acid/amine-based complexes

Molybdenum-squarate complex	Structure of the organic amine involved	Assignment <i>cis</i> -MoO ₂ ($\nu(\text{Mo}=\text{O}_i)$)	Assignment Mo–O bonds with organic ligand
A ^a	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{OH}$	945 (s), 918 (s)	549 (vs)
B ^a		946 (m), 917 (s), 901 (m)	607 (s), 546 (s), 529 (s)
C ^a		933 (s), 902 (s)	546 (vs)
D ^b		942 (s), 907 (s)	599 (s), 539 (w), 509 (w)
E ^b		940 (s), 915 (sh)	544 (vs)

^a Complexes prepared previously [18].

^b Newly prepared complexes.

on polyfunctional amines such as monoethanolamine, triethanolamine, guanidine and 1,3-diamino-2-propanol, generally believed to be stronger organic ligands than 1-phenyl-1-ethanamine (complex **D**), indicated strong absorptions within a rather narrow interval ($544\text{--}549\text{ cm}^{-1}$). Complex **B**, containing TEA with three hydroxyl functional groups, even showed three strong absorptions at 607, 546 and 529 cm^{-1} , respectively; similar phenomenon was observed with the characteristic bands for the *cis*-MoO₂ fragment ($946, 917, 901\text{ cm}^{-1}$). On the other hand, the specific structure of guanidine caused some shift of the bands assigned to the *cis*-MoO₂ fragment in complex **C** outside the common $940\text{--}946$ and $915\text{--}918\text{ cm}^{-1}$ intervals.

Some thermal analysis data for the salts and the corresponding molybdenum-containing complexes, dried in air for 24–48 h after their preparation are given in Table 5.

Again, as discussed in our previous publication [18], the temperatures, associated with the onset of decomposition for the newly synthesized squarate salts and the corresponding complexes were essentially lower than those of the pure squaric acid (H₂Sq). This indirectly proves the formation of

ammonium-type salts from the organic reactants. The temperature region of $400\text{--}500\text{ }^\circ\text{C}$ was, again, associated with the complete decomposition of squarate and this was clearly observed with both the complexes **D** and **E**. The comparison of some thermal analysis data for the molybdenum complex **C** prepared from H₂Sq and guanidine previously [18] with those of the newly synthesized complex **E** showed some interesting similarities. Both complexes were found to be somehow hygroscopic, with ca. 4% loss of water within nearly the same temperature interval ($40\text{--}150\text{ }^\circ\text{C}$). One possible explanation of this might be the more pronounced properties of guanidine and 1,3-diamino-2-propanol, participating in the formation of the corresponding complexes as stronger organic bases (Table 1). Guanidinium squarate and the complex **C**, however, showed higher thermal stability, estimated by the temperature region for the onset of decomposition. This was probably due to the fact that guanidine is still significantly stronger organic base than DAP (Table 1).

Based on the studies conducted so far, the following schemes for the preparation of the squarate salts can be postulated:

Table 5
Selected thermal analysis data for the organic salts and the corresponding molybdenum containing complexes based on squaric acid

Compound	Initial temperature interval (loss of water) ($^\circ\text{C}$)	Temperature region for the onset of decomposition ($^\circ\text{C}$)	Temperature region for the complete decomposition of organic matter ($^\circ\text{C}$)
H ₂ Sq	–	260–270	450–500
H ₂ Sq·2Gua·2H ₂ O ^a	75–160 (crystalhydrate)	225–230	–
Complex C ^a	40–160 (hygroscopic)	215–220	350–450
H ₂ Sq·2PhEA	–	160–170	–
Complex D	–	235–245	470–480
H ₂ Sq·DAP	–	200–210	–
Complex E	40–150 (hygroscopic)	160–200	400–500

^a Prepared previously [18].

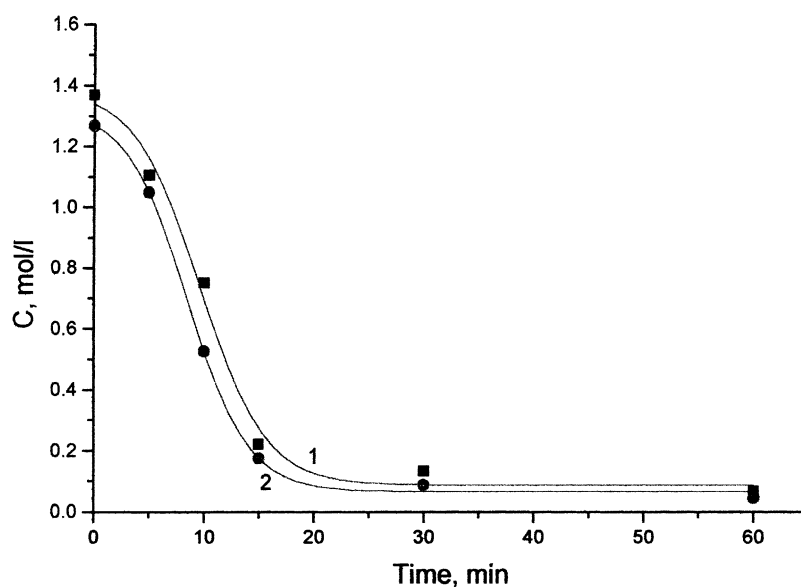
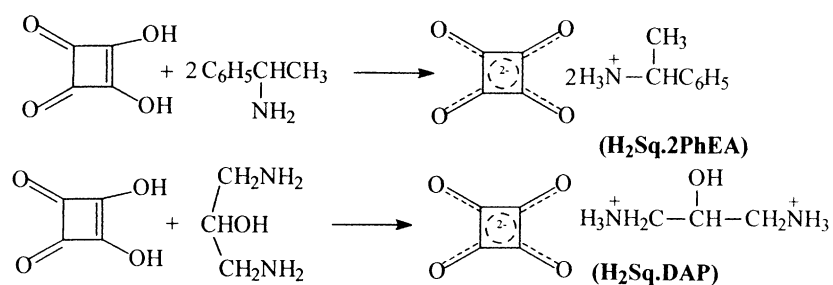


Fig. 1. Kinetic curves for the TBHP consumption for the epoxidation of cyclohexene in the presence of molybdenum-squarate complexes as catalysts: (1) Complex **D** and (2) complex **E**. Reaction conditions were as described in Section 2.

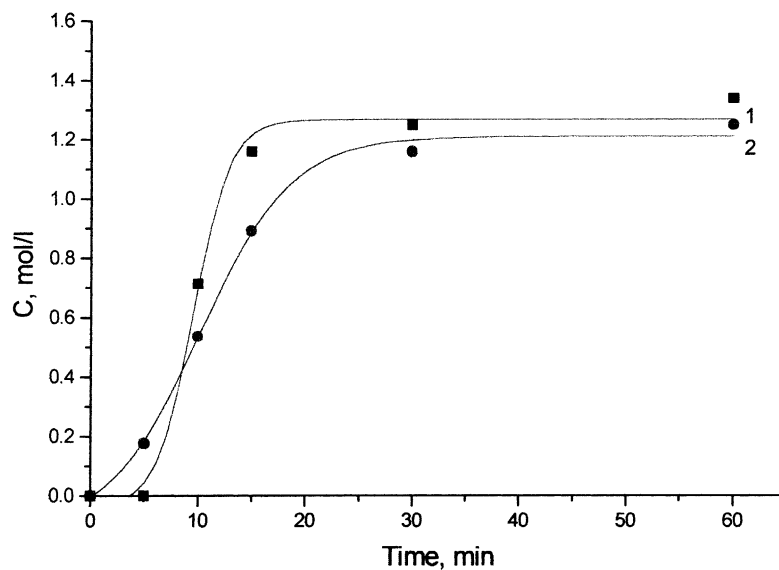


Fig. 2. Kinetic curves for the cyclohexene oxide accumulation for the epoxidation of cyclohexene in the presence of molybdenum-squarate complexes as catalysts: (1) Complex **D** and (2) complex **E**. Reaction conditions were as described in Section 2.

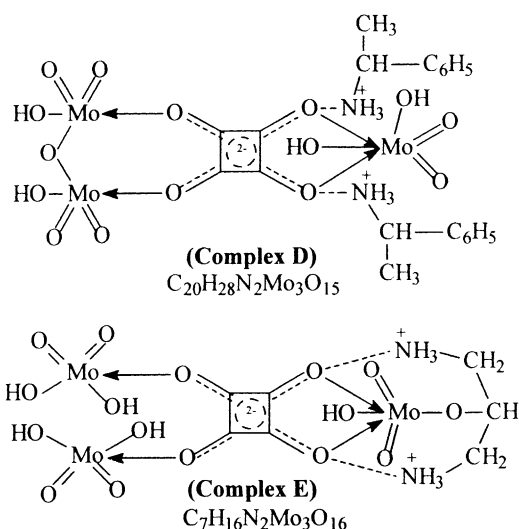
Table 6

Comparative evaluation of the activities and selectivities for some of the epoxidation catalysts^a prepared from H₂Sq, organic amines and MoO₂Cl₂

Type of catalyst (organic amine employed for its synthesis)	TBHP conversion (%) (reaction time, min)	Cyclohexene oxide final yield (%)	Turnover frequency (mol TBHP/mol Mo/min)
Complex A ^b (monoethanolamine)	97.2 (60)	96.1	23.2
Complex C ^b (guanidinium carbonate)	96.3 (60)	89.9	22.7
Complex D ^c (1-phenyl-1-ethanamine)	95.2 (60)	97.6	20.2
Complex E ^c (1,3-diamino-2-propanol)	96.5 (60)	98.3	20.0

^a Reaction conditions as described in Section 2.^b Prepared previously [18].^c Newly prepared.

The results from the FT-IR spectroscopy studies, combined with elemental analysis data and information on the behavior of MoO₂Cl₂ in solutions [30,31] allowed some suggestions on the possible structures of the molybdenum complexes prepared from H₂Sq, the amines and MoO₂Cl₂ in aqueous medium. Similar to our previous studies [18], relevant X-ray diffraction and mass spectrometry data were not obtained due to the poorly pronounced crystalline structure and the high metal content of the complexes respectively. This also caused some inconsistencies in the comparison of the “calculated” elemental analyses data with the experimental ones. Therefore, the proposed structures are speculative. The further studies will involve attempts to synthesize molybdenum complexes based on squaric acid and selected organic amines among those studied so far in *non-aqueous* medium in order to obtain appropriate crystalline products.



3.2. Catalytic epoxidations

Both the yields and selectivities in the epoxidation reactions were calculated as previously [18]. The catalytic activity was, again, evaluated by the turnover frequency, i.e. the maximum reaction rate observed with respect to TBHP per minute per active site of the catalyst and was, accordingly, expressed in appropriate units (e.g. mol TBHP reacted mol⁻¹ Mo min⁻¹). The molybdenum complexes be-

came soluble in the reaction medium under the experimental conditions and, therefore, acted as homogeneous catalysts.

The kinetic curves of TBHP consumption and cyclohexene oxide accumulation in the presence of the molybdenum complexes **D** and **E** as catalysts are shown in Figs. 1 and 2, respectively. Again, these molybdenum complexes indicated activities and selectivities, very close to some of those studied previously (Table 6) (the only exception in this respect was the molybdenum complex derived from H₂Sq and triethanolamine; the possible reasons for this have been discussed in our previous work [18]). GLC analyses showed cyclohexene oxide as the principal reaction product, together with an unreacted excess of cyclohexene, *tert*-butylalcohol (TBA) and 1–5% side (non-identified) products under the conditions of nearly complete TBHP conversion. The combination of highly mobile delocalized π -electron system and polarizable ions, derived from the involvement of the various ammonium squarate moieties and MoO₂²⁺ species in the complex structures probably contributed to the high catalytic activities observed. The catalytic activities and selectivities did not essentially depend on the structure of the amines employed. This fact and, also, the solubility of the catalysts under the reaction conditions suggest an intermediate coordination of the reactants and complete ligand exchange which occurred at the very beginning of the catalytic reaction.

4. Conclusions

Two novel molybdenum-containing complexes based on squaric acid, some organic amines of completely different structure and molybdenum dioxodichloride were synthesized by employing one-pot procedure in aqueous medium. The yields of the newly prepared molybdenum complexes were compared to those obtained, according to our previous publication and were found to depend on both the structure and properties of amines as organic bases. The applicability of these complexes as homogeneous catalysts for epoxidation of cyclohexene with organic hydroperoxides was proved. The newly prepared molybdenum-containing complexes showed almost the same catalytic activities and selectivities as those studied previously. Therefore, the structure of the amine, participating in the formation of the

molybdenum-squarate complex does not significantly affect the catalytic properties. This is believed to result from a complete ligand exchange, occurring at the onset of the epoxidation reaction.

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