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

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Abstract

Novel molybdenum-containing organic complexes based on 3,4-dihydroxy-3-cyclobutene-1,2-dione ("squaric acid") and some organic amines have been synthesized and characterized by infrared (IR) spectroscopy, thermogravimetric (TGA) and elemental analyses. The resulting molybdenum complexes were introduced as catalysts in the epoxidation of cyclohexene with *t*-butylhydroperoxide (TBHP) and showed high activities and selectivities, comparable to those of the commercially available molydenyl acetylacetonate ($MoO_2(acac)_2$).
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1. Introduction

Molybdenum-containing complexes have long been known to be 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-SiO$_2$ catalyst to effect the epoxidation of propylene to the synthetically useful propylene oxide precursor [1,2]. Since then, a number of soluble molybdenum-containing 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]. 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 [8–10].

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 unique position. Squaric acid is a strong dibasic acid with a four-atom ring framework endowed with hydrogen bonding (donor as well as acceptor) and ionic organizational features. Therefore, it appears particularly attractive as a template for generating self-assemblies from polarizable cations in general and organic bases in particular. 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 [11,12].

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It is therefore, believed that organic complexes formed by the interaction of squaric acid, some polyfunctional organic amines with chelating properties and Mo(VI) oxospecies would possess high catalytic activities and selectivities in the epoxidation reaction, due to the combination of highly mobile π-electron system and polarizable ions.

Squaric acid has been reported to give rise to a wide variety of complexes with transition metal compounds such as salts of nickel, cobalt and iron [13], uranium and titanium [14], vanadium [15,21], copper [16–18], etc. The similarities of the squarate anion to the oxalate one with respect to their structures and coordinative properties and its versatility as a ligand have also been discussed [17,18]. Publications on the preparation of molybdenum-containing complexes based on squaric acid have also emerged [19–21] but their syntheses were frequently associated with the use of expensive reagents and cumbersome procedures. No use of any organic transition metal complexes with squaric acid as catalysts for organic reactions has been reported so far, to the best of our knowledge.

Therefore, the aim of the present work was to attempt the preparation of some novel molybdenum complexes based on squaric acid by a simple and straightforward procedure, and to evaluate their applicability as catalysts for the epoxidation of cyclohexene by organic hydroperoxides.

2. Experimental

2.1. Starting materials

3,4-Dihydroxy-3-cyclobutene-1,2-dione (squaric acid, H_2Sq, 98%) was obtained from *Hulls-Marl* (Germany) and was recrystallized before use. 2-Aminoethanol (monoethanolamine, MEA) (BIOSYNT, *Riedel de Haen*, Germany), tris-(2-hydroxyethyl)amine (triethanolamine, TEA) (purum, *Fluka AG*), guanidinium carbonate Gua_2CO_3 (purum, ≥97%, *Fluka AG*) and molybdenum(VI) dioxodichloride (molybdenyl chloride, MoO_2Cl_2, *Aldrich*) were employed without further purification. Cyclohexene (*Merck-Schuchardt*, 99%), *t*-butyl hydroperoxide, TBHP (*Fluka AG*) and molybdenyl acetylacetonate $MoO_2(acac)_2$ (*Riedel de Haen*, Germany) were also used as received.

2.2. Syntheses of the molybdenum-containing complexes

2.2.1. Synthesis of the complex A

2.2.1.1. Preparation of monoethanolammonium squarate ($H_2Sq \cdot 2MEA$). The 0.342 g (3 mmol) squaric acid were placed into a small 50 ml beaker and then 5 ml distilled water were added. The suspension was slowly heated with stirring to 60–80 °C until the squaric acid was completely dissolved. Then 0.366 g (6 mmol) monoethanolamine, dissolved in 2 ml distilled water were quantitatively added to the hot solution and the stirring was continued for 2 h at room temperature. Slow evaporation for several days produced colourless to white needles, which were thoroughly filtered under vacuum and left to dry out in air for 24 h. Yield: 0.403 g, mp 130–131 °C. Anal. calcd for $C_8H_{16}N_2O_6$: C, 40.68; H, 6.77; N, 11.86. Found: C, 40.47; H, 6.70; N, 11.80. The following infrared absorptions were obtained in the 4000–400 cm^{-1} region (mid IR spectra, KBr pellets, cm^{-1}): 3093 (medium to strong, broad), 2999 (m), 2970 (m), 2947 (m), 2929 (m), 2851 (m), 2735 (w), 2637 (w), 2569 (w), 2528 (vw), 1610 (m), 1592 (m), 1545 (s), 1510 (s), 1463 (vs), 1453 (vs), 1426 (vs), 1384 (s), 1374 (s), 1300 (m), 1272 (m), 1135 (m), 1121 (m), 1105 (m), 1079 (s), 1014 (m), 966 (m), 868 (w), 817 (m), 796 (sh), 715 (w), 622 (vw), 530 (w).

Far infrared (far IR spectra, CsI pellets, 400–100 cm^{-1}): 387 (w), 352 (w), 337 (w), 316 (w), 248 (m), 165 (sh).

2.2.1.2. Synthesis of the molybdenum-containing complex (complex A). The 0.234 g (2.05 mmol) H_2Sq were placed into a small 50 ml beaker and 10 ml distilled water were added. The suspension was slowly heated with stirring between 60 and 80 °C until the squaric acid was completely dissolved. The 0.249 g (4.08 mmol) MEA, dissolved in 2 ml distilled water were added to the hot solution and the stirring was continued for 2 h at room temperature. This was followed by addition of 0.800 g (ca. 4 mmol) MoO_2Cl_2, which produced almost immediately a light green suspension and the latter soon began to gradually precipitate. Attempts to dissolve the product by careful heating to 60–70 °C were unsuccessful and the stirring was continued for another 12 h at

room temperature. Then the suspension was filtered under vacuum, washed consecutively and thoroughly with distilled water, acetone and ether and dried at room temperature in air. Yield: 0.650 g. Anal. calcd for $C_8H_{16}N_2Mo_4O_{18}$: C, 11.82; H, 1.97; N, 3.45; Mo, 47,29. Found: C, 11.57; H, 1.47; N, 3.62; Mo, 47.64. IR: 3420 (s, broad), 3250–3000, 2960 (w), 2924 (w), 2855 (w), 2800–2600, 1746 (vw), 1608 (s), 1574 (s), 1527 (vs), 1409 (m), 1377 (m), 1319, 1309 (doublet), 1259 (w), 1115, 1094 (doublet), 1061 (m), 996 (m), 945 (s), 918 (s), 875 (m, sh), 549 (vs), 426 (w).

Far IR: 398 (m), 368 (w), 322 (w), 281 (m), 228 (s), 217 (vs), 146 (w).

2.3. Synthesis of the complex B

2.3.1. Preparation of triethanolammonium squarate ($H_2Sq \cdot 2TEA$)

The 0.234 g (2.05 mmol) H_2Sq were placed into a small 50 ml beaker and 10 ml distilled water were added. The suspension was slowly heated with stirring to 60–80 °C until the squaric acid was completely dissolved. The 0.615 g (4.11 mmol) triethanolamine, dissolved in 2 ml distilled water were quantitatively added to the hot solution and the stirring was continued for 2 h at room temperature. Slow evaporation for almost a week produced colourless to white crystalline product which was filtered under vacuum and left to dry out in air for 24 h. Yield: 0.55 g, mp 83–85 °C, the product was rather hygroscopic. Anal. calcd for $C_{16}H_{32}N_2O_{10}$: C, 46.59; H, 7.84; N, 6.79. Found: C, 44.91; H, 8.55; N, 6.50. IR: 3473 (m, sh), 3377, 3355 (s, doublet), 3151 (m), 3008 (w), 2997 (w), 2967 (w), 2932 (w), 2902 (w), 2851 (w), 2671 and 2627 (broad), 1723 and 1710 (w, doublet), 1525 (vs), 1486 (m), 1458 (w), 1448 (w), 1435 (w), 1406 (m), 1354 (m), 1333 (m), 1321 (m), 1283 and 1268 (w, doublet), 1242 (m), 1231 (m), 1193 (sh), 1105 (m), 1095 (m), 1077 (m), 1034 (m), 1003 (m), 995 (m), 918 (m), 903 (w), 876 (w), 855 (vw), 843 (vw), 818 (s), 716 (w), 648 (vw), 530 (m).

Far IR: 360 (s), 314 (m), 266 (m), 222 (m), 202 (m), 178 (m), 135 (s).

2.3.2. Synthesis of the molybdenum-containing complex (complex B)

The 0.111 g (0.97 mmol) H_2Sq were placed into a small 50 ml beaker and then 5 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. The 0.306 g (2.05 mmol) TEA, dissolved in 2 ml distilled water were added to the hot solution and the stirring was continued for 2 h at room temperature. This was followed by addition of 0.396 g (ca. 2 mmol) MoO_2Cl_2 which produced almost immediately green suspension and the latter soon began to gradually deposit as precipitate. Attempts to dissolve the product by careful heating to 60–70 °C were unsuccessful and the stirring continued for another 12 h at room temperature. The suspension was filtered under vacuum, washed consecutively and thoroughly with distilled water, acetone and ether and dried at room temperature in air. Yield: 0.362 g. Anal. calcd for $C_{16}H_{34}N_2Mo_2O_{18}$: C, 26.16; H, 4.63; N, 3.81; Mo, 26.16. Found: C, 25.26; H, 4.82; N, 4.11; Mo, 26.70. IR: 3421 (m, sh), 3344 (vs), 3313 (vs), 3159 (s), 3100 (w), 2975 (w), 2938 (m), 2903 (m), 2846 (m), 2795 (m), 2724 (w), 2686 (w), 2614 (w), 2501 (w), 1570 (s), 1533 (s), 1488 (m), 1460 (m), 1405 (s), 1369 (w), 1328 (m), 1304 (w), 1258 (w), 1199 (w), 1096 (m), 1080 (m), 1068 (w), 1031 (s), 1006 (m), 947 (m), 917 (s), 846 (w), 608 (m), 548 (s), 427 (w).

Far IR: 396 (s), 367 (m), 325 (w), 311 (vw), 281 (m), 230 (s), 214 (m), 209 (w), 146 (w).

2.4. Synthesis of the complex C

2.4.1. Preparation of guanidinium squarate dihydrate $H_2Sq \cdot 2Gua \cdot 2H_2O$

The 0.337 g (2.96 mmol) H_2Sq were placed in a 50 ml beaker and 10 ml distilled water were added. The suspension was slowly heated with stirring to between 60 and 80 °C until the squaric acid was completely dissolved. The 0.533 g (2.96 mmol) guanidinium carbonate (Gua_2CO_3) were gradually added to the hot solution until the evolution of carbon dioxide ceased and the stirring continued for 1 h at room temperature. Small needle-shaped colourless crystals were gradually formed on cooling and slow evaporation of the solution which were further purified by recrystallization from water. Yield: 0.635 g. Anal. calcd for $C_6H_{16}N_6O_6$: C, 26.86; H, 5.97; N, 31.3. Found: C, 25.89; H, 5.77; N, 30.51.

IR: 3618 (m), 3580 (w), 3547 (w), 3446 (m), 3435 (m), 3385 (w), 3290 (w), 3280 (w), 3182 (w, broad), 1817 (w), 1703 (m), 1636 (m), 1576 (m), 1485 (m),

1476 (m), 1408 (vs), 1155 and 1145 (w, doublet), 1072 (w), 1045 (vw), 926 (w), 852 (vw), 832 (m), 707 (w), 628 (m), 444 (m).

Far IR: 356 (m), 248 (m), 195 (sh), 166 (s), 155 (sh).

2.4.2. Synthesis of the molybdenum-containing complex (complex C)

The 0.228 g (2 mmol) H_2Sq were placed in a 50 ml beaker and 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. The 0.360 g (2.00 mmol) Gua_2CO_3 were gradually added to the hot solution until the evolution of carbon dioxide ceased. The stirring continued with occasional heating to maintain the product in solution, for approximately 0.5 h and then 0.796 g (ca. 4.00 mmol) MoO_2Cl_2 were carefully added to the hot solution. Further stirring for another hour, followed by cooling to room temperature produced light green suspension which soon began to gradually deposit as precipitate. The latter was filtered under vacuum, washed consecutively and thoroughly with distilled water, acetone and ether and dried at room temperature in air. Yield: 0.742 g. Anal. calcd for $C_6H_{14}N_6Mo_4O_{16}$: C, 8.87; H, 1.73; N, 10.37; Mo, 47.40. Found: C, 9.22; H, 1.13; N, 10.16; Mo, 45.67. IR: 3550 (m, sh), 3428 (vs), 3268 (m), 3195 (m), 2961 (w), 2924 (w), 2853 (w), 1808 (vw), 1668 (s), 1602 (w), 1521 (vs), 1115 and 1093 (w, doublet), 933 (s), 902 (s), 546 (vs), 468 (sh), 422 (w).

Far IR: 392 (m), 371 (w), 324 (w), 281 (m), 230 (s), 220 (s), 215 (sh), 157 (w).

2.5. 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.

2.6. 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 (polydimetylsiloxane) 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 [22] 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 MoO_3 at 650–700 °C with the complete loss of organic matter [26]. The IR spectrum of the inorganic residue was identical to that of commercial MoO_3. The results from the TGA were found to correspond to those obtained from the colorimetric method for molybdenum analysis, based on the formation of coloured complexes with thiocyanate [23]. 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). Both the medium and far FT-IR spectra of the samples were run on *Bruker IFS-113* spectrometer as KBr and CsI pellets in the 4000–400 and 400–100 cm⁻¹ regions, respectively.

3. Results and discussion

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

The initial attempts to prepare molybdenum-containing complexes by the direct interaction of H_2Sq

or its sodium salt with MoO_2Cl_2 or by prolonged heating of MoO_3 with H_2Sq in aqueous medium did not produce satisfactory results. The reason for this is likely due to the poor dissociation of H_2Sq in the aqueous solution of MoO_2Cl_2, which itself produces a highly-acidic medium on one hand, and the very low solubility of MoO_3 in water, on the other. In both cases, predominant formation of H_2MoO_4 or "molybdenum blue" occurred instead. Therefore, further work was concentrated on introducing other reactants such as polyfunctional amines into the reaction system. It was anticipated that these organic bases, acting as additional reactants and reducing the acidity, would utilize the potential of H_2Sq as a ligand in more favourable direction. In the course of the studies, it was recognized that if H_2Sq, the organic amine and MoO_2Cl_2 were consecutively introduced in the reaction in one single step (one-pot procedure), the formation of the corresponding complexes would be favoured. However, the preparation of the squaric acid salts with the organic bases was also conducted separately in order to prove their formation in the aqueous solution and to compare their spectral characteristics with those of the corresponding molybdenum complexes.

The salts of H_2Sq with the organic bases were found to be crystalline compounds. Only the guanidinium salt ($H_2Sq·2Gua·2H_2O$) was characterized and found to be crystallohydrate by TGA/DTA analysis and no melting phenomena were detected. The salts $H_2Sq·2MEA$ and $H_2Sq·2TEA$, containing hydroxyethyl fragments had sharp melting temperatures. The molybdenum-containing complexes, on the other hand, were barely soluble in water and some of the commonly used inert organic solvents even at elevated temperatures and did not have pronounced crystalline structures. This prevented us from obtaining samples for X-ray diffraction analysis in order to conduct their full structural characterization. Both the middle and far IR spectra of the organic salts and the corresponding molybdenum-containing complexes, prepared in aqueous solution showed the characteristic fundamental vibrations near 1530, 1090, 350 and 259 cm^{-1}. These vibrations have been established for the squarate anion (SQ^{2-}) of high (D_{4h}) symmetry in the IR spectra of potassium, sodium and lithium squarates [24,25]. 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 [16]. Thus, the squarate ion in the molybdenum complexes functions as bis-bidentate bridging ligand. The elemental analysis proved the stoichiometry in the formation of the organic salts. The quantitative determination of nitrogen showed that the polyfunctional 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. H$_2$Sq·2MEA and complex A

The current search in the literature did not reveal any reports for the preparation and characterization of the monoethanolammonium salt $H_2Sq·2MEA$ and its corresponding transition metal complexes. The corresponding wavenumbers (cm^{-1}) of the observed characteristic bands in the IR spectra and their assignments [27] for $H_2Sq·2MEA$ and complex A are listed in Table 1.

The broad multiplet band between 2700 and 2000 cm^{-1} and the lack of pronounced absorptions within 3500–3100 cm^{-1} are typical for the ammonium (–NH$_3^+$-type) salts such as $H_2Sq·2MEA$. The sequence of several strong absorptions between 1470 and 1370 cm^{-1} ($\delta(CH_2)$) in $H_2Sq·2MEA$ resulted from the considerable split of the typical bands for the methylene groups, due to the presence of the (CH$_2$–NH$_3^+$) fragment. No bands at 1790–1820 cm^{-1}, usually assigned to the localized C=O bonds (free non-coordinated carbonyl) in the squaric acid and at 1630–1690 cm^{-1} ($\nu(C=C)$ in H_2Sq) [21] were detected. This also proved the presence of the squarate anion (SQ^{2-}) moiety in the organic salt and the corresponding complex. The interaction with MoO_2Cl_2 resulted in some essential changes in the spectrum of complex A with respect to that of $H_2Sq·2MEA$. The fundamental bands for SQ^{2-} (1545 and 1510 cm^{-1} in $H_2Sq·2MEA$) emerged as a single strong absorption at 1527 cm^{-1} in the molybdenum complex A. The strong bands at 945 and 918 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 ($\nu(Mo=O_t)$), as reported in a number of publications [19–21,26]. It is known that, within the region of 400–600 cm^{-1}, metal-oxygen stretching

Table 1
Selected vibrational data (cm^{-1}) and their assignment for H$_2$Sq·2MEA and complex A

H$_2$Sq·2MEA		Complex A	
Wavenumbers	Assignment	Wavenumbers	Assignment
3093	ν(OH), ν(NH$_3$)$^+$	3425	ν(OH)
2999, 2970, 2947, 2929, 2851	ν(CH$_2$), ν(CH$_2$OH)	2960, 2924, 2855	ν(CH$_2$)
2735, 2637, 2569 (broad, muliplet)	ν(NH)$^+$, associated, salt "bridges", NH$^+\cdots$O$^-$, etc.	2748, 2649, 2237 (broad, multiplet)	ν(NH)$^+$, associated, salt "bridges", NH$^+\cdots$O$^-$, etc.
1610, 1592	δ(NH$_3$)$^+$	1608, 1574	δ(NH$_3$)$^+$
1545, 1510	ν(C–O) + ν(C–C), SQ^{2-}	1527	ν(C–O) + ν(C–C), SQ^{2-}
1463 (sh), 1453, 1426, 1384, 1374 (sh)	δ(CH$_2$), δ(CH$_2$OH), δ(CH$_2$–N), δ(OH)	1409, 1377, 1319, 1309, 1259	δ(CH$_2$), δ(CH$_2$–N), ω(CH$_2$)
1305, 1272	ω(CH$_2$), ω(CH$_2$OH)		
1135, 1105	ν(C–O), ν(C–N), ρ(NH$_3$)$^+$	1115, 1094	ν(C–O), ν(C–N), ρ(NH$_3$)$^+$
1079	SQ^{2-}, ν(C–O), ν(C–N), ρ(NH$_3$)$^+$	1061, 996	SQ^{2-}, ν(C–O), ν(C–N), ρ(NH$_3$)$^+$, ν(C–C)/ρ(NH$_3$)$^+$
1014, 966	ν(C–C)/ρ(NH$_3$)$^+$	945, 918	*cis*-MoO$_2$ (ν(Mo=O$_t$))
868, 817, 796	ρ(CH$_2$), ρ(CH$_2$OH)	875, 822	ρ(CH$_2$)
530	C–C–O (skeletal)	549	Mo–O bonds with O-containing organic ligand
353	δ(C–O) + δ(C–C), SQ^{2-}	369	SQ^{2-}
317	C–C (skeletal) for the organic cation	282	–
248	γ(C–O) + γ(C–C), SQ^{2-}	228, 217	δ(O–Mo–O) and δ(O–Mo–O)

vibrations are metal-sensitive and are shifted to higher frequencies in the order Ni(II) < Cu(II) < V(III), etc. [15,17]. Thus, the formation of polar Mo–O bond with the organic ligands [26] resulted in the appearance of a new strong band observed in the spectrum of complex A at 549 cm^{-1}. Finally, the new very strong bands emerging as a doublet at 228 and 217 cm^{-1} in the far IR spectrum of the complex A can be assigned to O–Mo=O and O–Mo=O bending vibrations but further evidences for this are deemed necessary.

3.1.2. H$_2$Sq·2TEA and complex B

H$_2$Sq·2TEA and its molybdenum-containing complex (B) are also novel compounds. The corresponding wavenumbers (cm^{-1}) of the observed characteristic bands in the IR spectra and their assignments [27] are listed in Table 2.

The formation of the molybdenum-containing complex B was associated with some shift of the bands at 3500–3300 cm^{-1} (ν(OH)) to lower frequencies, compared to H$_2$Sq·2TEA. This was due to the involvement of hydroxyl groups in the complex formation (Table 2). The formation of ammonium

($>$NH$^+$) salt was proved by the broad multiplet absorption within 2700–2200 cm^{-1} observed for these products. The fundamental strong band for SQ^{2-} in H$_2$Sq·2TEA (1525 cm^{-1}) was split into two weaker bands at 1572 and 1532 cm^{-1} in complex B. This points to the decrease in the typical D_{4h} symmetry for the squarate as a result of its coordination to the oxomolybdenum fragment. The new band at 946 cm^{-1} detected for the molybdenum-containing complex only is assigned to the *cis*-MoO$_2$ fragment (ν(Mo=O)). The other *cis*-MoO$_2$ absorption at 915–920 cm^{-1} overlapped the band at 918 cm^{-1} (ρ(CH$_2$OH) in H$_2$Sq·2TEA) and strongly increased its intensity. The very strong absorptions at 607, 546 and 529 cm^{-1} (some of them overlapping the γ(OH) band) are attributed to the formation of strongly polar Mo–O bonds with several organic ligand functional groups [26]. The fundamental vibrations for SQ^{2-} of H$_2$Sq·2TEA in the far IR region at 361 and 267 cm^{-1} were also shifted towards higher wavenumbers and changed their intensities in complex B with the coordination to the MoO$_2$-fragment. As stated above, the very strong bands at 230 cm^{-1} combined with the one at 214 cm^{-1} for the complex B can probably

Table 2
Selected vibrational data (cm^{-1}) and their assignment for H$_2$Sq·2TEA and complex B

H$_2$Sq·2TEA		Complex B	
Wavenumbers	Assignment	Wavenumbers	Assignment
3473, 3377, 3355, 3151	ν(OH), H-bonds	3421, 3344, 3313, 3159	ν(OH), H-bonds
3008, 2997, 2967, 2902, 2851	ν(CH$_2$), ν(CH$_2$OH)	3010, 2975, 2938, 2903, 2846	ν(CH$_2$), ν(CH$_2$OH)
2700–2000 (broad, multiplet)	ν(NH)$^+$, associated, salt "bridges", NH$^+\cdots$O$^-$, etc.	2700–2400 (broad, multiplet)	ν(NH)$^+$, associated, salt "bridges", NH$^+\cdots$O$^-$, etc.
1525	ν(C–O) + ν(C–C), SQ^{2-}	1572, 1532	SQ^{2-}
1486, 1458, 1448, 1435	δ(CH$_2$), δ(CH$_2$OH), δ(CH$_2$–N)	1488, 1460, 1439	δ(CH$_2$), δ(CH$_2$OH), δ(CH$_2$–N)
1406	δ(OH)	1402	δ(OH)
1354, 1333, 1321, 1283, 1268, 1242, 1231	ω(CH$_2$OH), ω(CH$_2$), τ(CH$_2$), τ(CH$_2$OH), etc.	1369, 1327, 1304, 1258, 1248, 1233, 1197	ω(CH$_2$OH), ω(CH$_2$), τ(CH$_2$), τ(CH$_2$OH), etc.
1105, 1095, 1077,	SQ^{2-}, ν(C–O), ν(C–N)	1096, 1081, 1067	SQ^{2-}, ν(C–O), ν(C–N)
1034, 1003, 995	ν(C–C)	1032, 1006	ν(C–C)
918, 903, 876, 796	ρ(CH$_2$), ρ(CH$_2$OH)	946, 917, 901	cis-MoO$_2$ ν(Mo=O$_t$)) ρ(CH$_2$), ρ(CH$_2$OH)
642	γ(OH)	607, 546, 529	Mo–O bonds with organic ligands
540, 526, 508	C–C–O (skeletal)		
423	C–C (skeletal)	423	C–C (skeletal)
361, 267	δ(C–O) + δ(C–C), γ(C–O) + γ(C–C), SQ^{2-}	367, 281	SQ^{2-}
314	C–C (skeletal) for the organic cation	325	C–C (skeletal) for the organic cation
222, 202, 178	Twisting vibrations for the organic cation	230, 214	δ(O=Mo–O) and δ(O–Mo–O)

be assigned to O–Mo=O and O–Mo–O bending vibrations.

3.1.3. H$_2$Sq·2Gua·2H$_2$O and complex C

The preparation and the crystalline structure of guanidinium squarate dihydrate have been studied previously [28]. The corresponding wavenumbers (cm^{-1}) of the observed characteristic bands in the IR spectra and their assignments [27] are listed in Table 3.

Compared to the other squarates, the IR spectrum of H$_2$Sq·2Gua·2H$_2$O contained fewer absorption bands due to the high symmetry of the guanidinium cation (C(NH$_2$)$_3$$^+$, D_{3h}) and squarate anion (SQ^{2-}, D_{4h}). The formation of the molybdenum complex C was associated with some shift and broadening of the band at 3413 cm^{-1} (ν(OH)) due to the crystallohydrate water in H$_2$Sq·2Gua·2H$_2$O towards higher frequencies (Table 3). Moreover, two new and distinct bands at 3268 and 3195 cm^{-1} emerged, which can be attributed to stretching N–H vibrations of the guanidinium cation [C(NH$_2$)$_3$]$^+$, affected by the complex forma-

tion. The bands at 3000–2200 cm^{-1} were assigned to N–H$\cdots$O hydrogen bonds of various strength in both the guanidinium salt and complex. The X-ray diffraction studies on H$_2$Sq·2Gua·2H$_2$O conducted earlier proved that all hydrogen atoms of the guanidinium cation were involved in formation of hydrogen bonds with the squarate anion SQ^{2-} [28]. The mixed vibrations (δ(NH$_2$) and ν(C–N), delocalized) at 1697 and 1659 cm^{-1} in H$_2$Sq·2Gua·2H$_2$O were transformed into a new single (non-split) band at 1668 cm^{-1} in complex C (change in the symmetry). On the other hand, the band at 1147 cm^{-1} for H$_2$Sq·2Gua·2H$_2$O was considerably shifted to 1115 cm^{-1} in complex C and its intensity was reduced. This also proves the coordination of the guanidinium moiety to the MoO$_2$ fragment. The fundamental strong vibrations for SQ^{2-} at 1510–1530 and 1100–1090 cm^{-1} were observed in both the salt and complex. Again, the strong bands at 933 and 902 cm^{-1} present in the molybdenum-containing complex only can be definitely assigned to the cis-MoO$_2$ fragment. The formation of strongly polar Mo–O bond with an organic

Table 3
Selected vibrational data (cm^{-1}) and their assignment for $H_2Sq\cdot2Gua\cdot2H_2O$ and complex C

$H_2Sq\cdot2Gua\cdot2H_2O$		Complex C	
Wavenumbers	Assignment	Wavenumbers	Assignment
3413	ν(OH), H-bonds (crystallohydrate)	3550 (sh), 3428	ν(OH), H-bonds (crystallohydrate)
3143	ν(NH) for $C(NH_2)_3^+$	3268, 3195	ν(NH) for $C(NH_2)_3^+$
3000–2200	$\nu(NH_2)^+$, associated, salt	3000–2200	$\nu(NH_2)^+$, associated, salt
(broad multiplet)	"bridges", $NH^+\cdots O^-$, etc.	(broad multiplet)	"bridges", $NH^+\cdots O^-$, etc.
1697, 1659, 1596	$\delta(C(NH_2)_3^+)$ $\delta(NH_2)$ and ν(C–N))	1668, 1602	$\delta(C(NH_2)_3^+)$, ($\delta(NH_2)$ and ν(C–N))
1510	ν(C–O) + ν(C–C), SQ^{2-}	1521	SQ^{2-}
1147	$\delta(NH_2)$	1115	$\delta(NH_2)$
1098	ν(C–O) + ν(C–C), SQ^{2-}	1093	SQ^{2-}
742, 671, 633, 564, 539, 426	$\gamma(NH_2)$ for $C(NH_2)_3^+$	933, 902, 546, 468 (sh), 422	*cis*-MoO_2 (ν(Mo=O_t)), Mo–O bonds with organic ligands, $\gamma(NH_2)$ for $C(NH_2)_3^+$
356, 249	δ(C–O) + δ(C–C), γ(C–O) + γ(C–C), SQ^{2-}	392, 371, 282, 230, 220	Mo–O-organic ligand (bending) SQ^{2-} δ(O=Mo–O) and δ(O–Mo–O)

ligand (most probably, the squarate moiety) resulted in one of the strongest band observed in the spectrum of complex C at $546\,cm^{-1}$. The new strong absorption at $390–400\,cm^{-1}$ in the far IR spectrum of complex C, observed also in the spectra of the other complexes could probably be associated with Mo–O bending vibrations. In this case, the latter are, perhaps, combined with modes of vibration, characteristic of the Mo–N coordination. The considerable shift and changes in the fundamental vibrations for SQ^{2-} (371 and $282\,cm^{-1}$ versus 356 and $249\,cm^{-1}$ for the salt, respectively) can serve as additional evidence for the coordination of squarate to the MoO_2 fragment. Once again, the very strong bands at $230–220\,cm^{-1}$ for the complex C perhaps correspond to O–Mo=O and O–Mo–O bending vibrations.

In all cases discussed above concerning the complexes A, B and C, the characteristic doublets (sometimes with shoulders) observed in the $900–950\,cm^{-1}$ region and attributed to the *cis*-MoO_2 fragment were of a high analytical value. The positions and the intensities of the corresponding bands depended strongly on the kind of the organic amine involved in the complex formation.

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 4.

The temperatures, associated with the onset of decomposition for all compounds studied were essentially lower than those of the pure squaric acid (H_2Sq). This indirectly proves the formation of

Table 4
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; °C)	Temperature region for the onset of decomposition (°C)	Temperature region for the complete decomposition of organic matter (°C)
H_2Sq	–	260–270	450–500
$H_2Sq\cdot2MEA$	–	160–165	–
Complex A	50–200 (hygroscopic)	200–210	450–500
$H_2Sq\cdot2TEA$	–	200–210	–
Complex B	60–140	170–180	660–750
$H_2Sq\cdot2Gua\cdot2H_2O$	75–160 (crystallohydrate)	225–230	–
Complex C	40–160 (hygroscopic)	215–220	350–450

ammonium-type salts from the organic reactants. The guanidinium salt and the corresponding complex C had the highest thermal stability in this respect. This is not surprising, bearing in mind that guanidine is one of the strongest organic bases, forming very strong ionic and hydrogen bonds with H_2Sq. The temperature region of 350–500 °C is associated with the complete decomposition of squarate anion and this was clearly observed with complexes A and C. Complex B, however, showed completely different mode

of thermal degradation, i.e. it decomposed gradually from 170 to 750 °C. One possible explanation for this might be that, whereas the triethanolammonium salt bond is probably the least thermally stable fragment in the complex, the strongly polar Mo–O bonds of MoO_2^{2+} with more than one oxyethyl groups in the TEA moiety caused the gradual thermal degradation of the organic matter.

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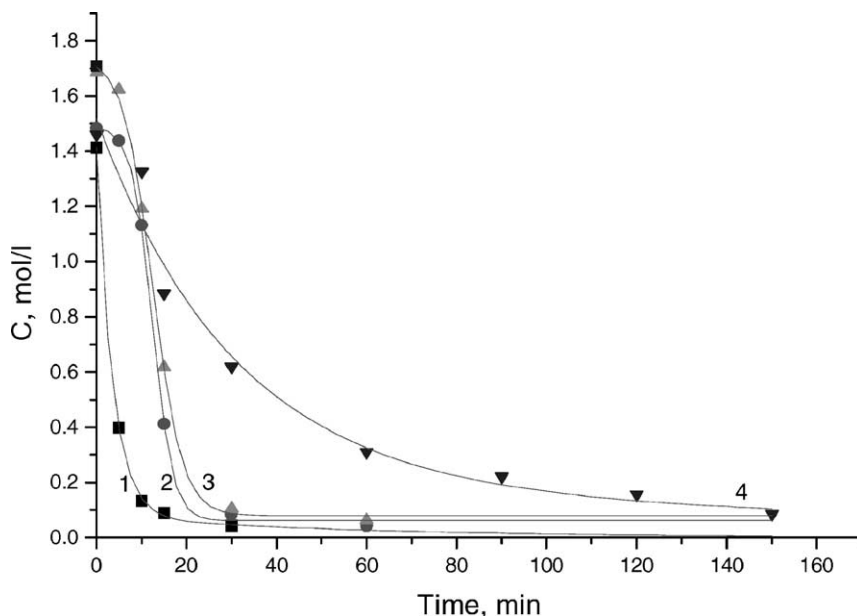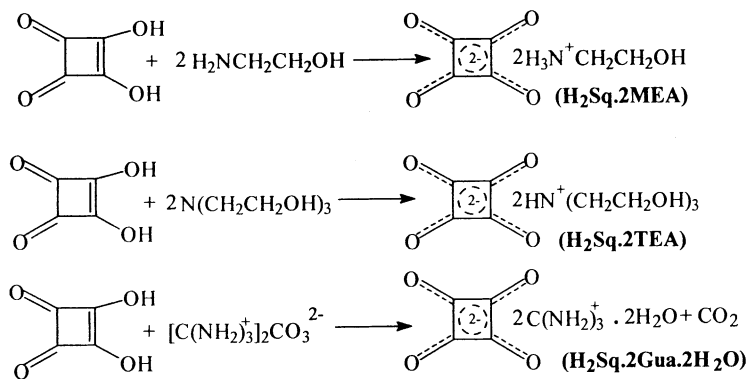

Fig. 1. Kinetic curves for the TBHP consumption in the epoxidation of cyclohexene in the presence of various molybdenum complexes as catalysts. (1) $MoO_2(acac)_2$; (2) complex A; (3) complex C; (4) complex B. Reaction conditions were as described in the experimental part.

The results from the FT-IR spectroscopy studies, combined with elemental analysis data and information on the behaviour of MoO_2Cl_2 in solutions [29,30] allowed some suggestions on the possible structures of the molybdenum complexes prepared from H_2Sq, polyfunctional amines and MoO_2Cl_2 in aqueous medium. Unfortunately, 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. Therefore, the proposed structures are speculative and further studies on the synthesis of similar molybdenum complexes in *non-aqueous* medium in attempts to obtain appropriate crystalline products are considered necessary.
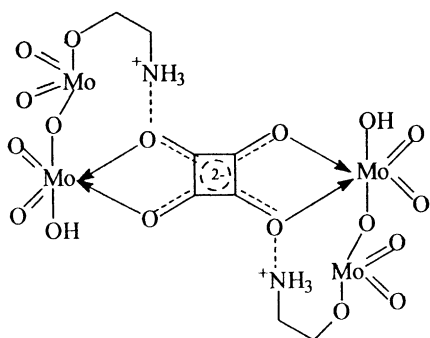
(Complex A) $C_8H_{16}N_2Mo_4O_{18}$
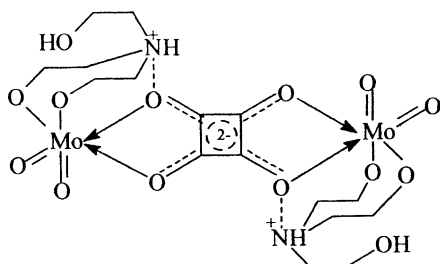
(Complex B) $C_{16}H_{28}N_2Mo_2O_{14}$
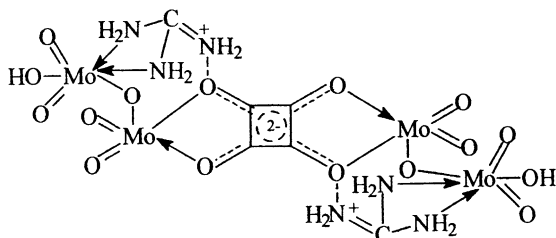
(Complex C) $C_6H_{14}N_6Mo_4O_{16}$

3.2. Catalytic epoxidations

The yields in the reactions are expressed as $Y = (C_{ox}/C_o) \times 100$ where C_{ox} and C_o $(mol\,l^{-1})$ are the concentration of epoxide formed and the initial concentration of TBHP, respectively. The selectivity with respect to the TBHP reacted was calculated by the ratio $S = 100 \times C_{ox}/(C_o - C)$, where C is the final TBHP concentration. In most cases, the latter was found to be 95–100%. The catalytic activity was 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}). An excess of cyclohexene with respect to TBHP (molar ratio of 6–7) was used in order to obtain high TBHP conversions and selectivities with respect to cyclohexene oxide. No inert solvent was employed, since the objective of this study was to estimate the catalytic activity, selectivity and versatility under more "severe" conditions (i.e. higher concentrations of both reactants). The molybdenum complexes became soluble in the reaction medium under the experimental conditions and, hence, acted as homogeneous catalysts. This is probably caused by the intermediate coordination with the reactants and ligand exchange.

The kinetic curves of TBHP consumption and cyclohexene oxide accumulation in the presence of the various molybdenum complexes as catalysts are shown in Figs. 1 and 2, respectively.

For the commercial $MoO_2(acac)_2$, nearly complete TBHP conversion and high cyclohexene oxide yield were reached within shorter reaction times, compared to the molybdenum complexes based on H_2Sq. Nevertheless, the catalytic activities, evaluated also by the turnover frequencies and the reaction yields with respect to cyclohexene oxide for the newly synthesized molybdenum complexes were high enough, as shown in Table 5.

Since the active species in epoxidation of alkenes by organic hydroperoxides catalyzed by dioxomolybdenum(VI) complexes contains hydroperoxide, coordinated to the metal via one of its oxygen atoms [31], it is necessary for a ligand to dissociate in order to create the corresponding vacant site. In our case, multidentate ligand(s) such as the aromatic and stable squarate anion, guanidinium fragment, etc. in which more than one of the donor atoms are only weakly
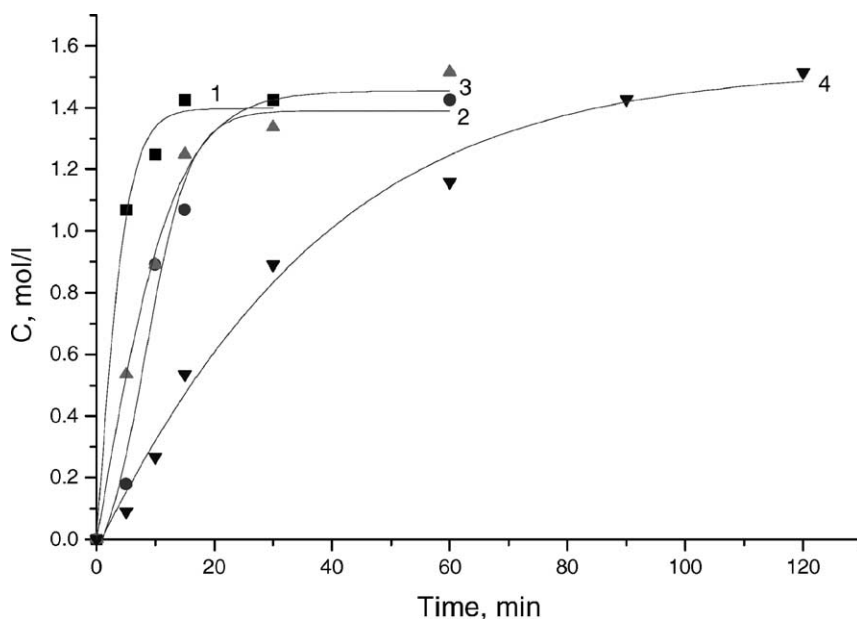
Fig. 2. Kinetic curves for the cyclohexene oxide accumulation in the epoxidation of cyclohexene in the presence of various molybdenum complexes as catalysts. (1) $MoO_2(acac)_2$; (2) complex A; (3) complex C; (4) complex B. Reaction conditions were as described in the experimental part.

bound to the molybdenum centre, were employed, resulting in an efficient coordination of TBHP. Moreover, the combination of highly mobile delocalized π-electron system and polarizable ions, derived from the involvement of the various ammonium squarate moieties and MoO_2^{2+} species in the complex structures probably contributed to the high catalytic activities observed. These speculations are consistent with the fact that, whereas complexes A and C with MEA and guanidinium as additional ligands showed nearly the same catalytic activities (Figs. 1 and 2), complex

B with TEA was less active and more side products were formed (Table 5). With complex B, the presence of Mo–O polar covalent bonds with, perhaps, two oxygen atoms of TEA and the "free" hydroxyethyl moiety are believed to create some "rigidity" in the structure and "inhibition" of the reaction. In all cases, GLC analysis showed cyclohexene oxide as the major reaction product, together with the unreacted excess of cyclohexene and *tert*-butylalcohol (TBA) under the conditions of nearly complete TBHP conversion (Table 5). For the reaction catalyzed by

Table 5
Comparative evaluation of the activities and selectivities for the epoxidation catalysts[a]

Type of catalyst	TBHP conver-sion (%), (reaction time, min)	Cyclohe-xene oxide final yield (%)	Turnover frequency (mol TBHP/mol Mo/min)	Reaction products (%)			
				TBA	Cyclohe-xene	Cyclohe-xene oxide	Others
MoO_2 (acac)$_2$	96.9 (30)	99.5	45.4	5.8	79.4	12.5	2.3
Complex A	97.2 (60)	96.1	23.2	2.9	84.8	10.6	1.7
Complex C[b]	96.3 (60)	89.9	22.7	6.2	81.4	11.2	1.2
Complex B	94.2 (150)	103.9	7.8	9.5	60.0	18.8	11.5

[a] Reaction conditions as described in the experimental part.
[b] 1.1 ml TBHP added to the reaction mixture, instead of 1 ml.

complex B, certain amounts of side products such as 2-cyclohexene-1-ol and 2-cyclohexene-1-one (up to 11–12%), accompanied by cyclohexene oxide yield, unexpectedly higher than 100% were detected. This is probably caused by the intervention of molecular oxygen as an *additional* oxidant under the conditions of prolonged catalytic reaction. Thus, the calculated ratio between the final concentration of cyclohexene oxide and the initial TBHP concentration, determining the final yield of epoxide *with respect to TBHP* exceeded 100%, as observed also in other publications [10,32,33].

4. Conclusions

Three novel molybdenum-containing complexes based on squaric acid, organic amines and molybdenum dioxydichloride were synthesized by employing one-pot procedure in aqueous medium. The applicability of these complexes as homogeneous catalysts for epoxidation of cyclohexene with organic hydroperoxides was proved.

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