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Synthesis and crystal and molecular structure of $[(n\text{-}C_4H_9)_4N]_2[MoO_2(C_5O_5)_2]$; confirmation of exclusively η^2-coordination by a croconate ligand

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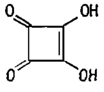
Abstract

The reaction of $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_7]$ with BaC_5O_5 in acetonitrile yields red crystals of $[(n\text{-}C_4H_9)_4N]_2[MoO_2(C_5O_5)_2]$. The compound crystallizes in the monoclinic space group $C2/c$ with $a=36.502(11)$, $b=14.681(3)$, $c=18.109(5)$ Å, $\beta=93.84(1)°$, $V=9682.5(15)$ Å^3, $D_{calc}=1.22$ g cm^{-3} for $Z=8$. Structure solution and refinement based on 3593 reflections with $F_o \geqslant 6\sigma(F_o)$ Mo Kα, $\lambda=0.71073$ Å) converged at 0.0693. The structure of the anion consists of a mononuclear Mo(VI) center in a distorted octahedral environment of the *cis*-oxo groups and the oxygen donors of two bidentate croconate ligands. The 1,2-chelating geometry of the croconate is unusual in that all previously structurally characterized examples of croconate coordination exhibit additional bonding to a second metal site via the oxygen donor in the 4 position.

Introduction

As part of our continuing investigations of the chemistry of polyoxomolybdates with oxygen donor ligands [1–11], we have recently focused on the interactions of molybdates with 'oxocarbons' [12–16]. The term oxocarbon designates compounds in which all of the carbon atoms are bonded to carbonyl or enolic oxygens or to their hydrated or depronated equivalents [17]. The chemistry of polyoxomolybdates with squaric acid (1) and rhodizonic acid (3) revealed several unusual cluster types and ligand transformations. Since the chemistry of the third member of this series, croconic acid (2), with polyoxomolybdates has not been reported, we undertook an investigation of the reactions of $Mo_2O_7^{2-}$ with croconate. In this paper, the preparation and structure of $(n\text{-}C_4H_9)_4N]_2[MoO_2(C_5O_5)_2]$ are reported.



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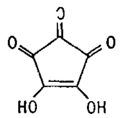

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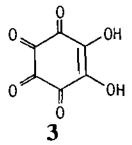

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Experimental

Materials and methods

All reactions were performed in freshly dried and distilled solvents under an atmosphere of argon. Dichloromethane was technical grade and was distilled from $CaCl_2$ and P_4O_{10}. BaC_5O_5 was prepared by the literature method [18].

The following instruments were used in the study: IR, Perkin-Elmer 283B IR spectrophotometer; X-ray crystallography, Siemens R3m/V diffractometer.

Preparation of $[(n\text{-}C_4H_9)_4N]_2[MoO_2(C_5O_5)_2]$

A solution of BaC_5O_5 (5.55 g, 20 mmol) in acetonitrile (25 ml) was added to a stirred solution of $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_7]$ (7.88 g, 10 mmol) in methylene chloride (50 ml). Upon addition of diethyl ether, a copious red precipitate was formed. Recrystallization from acetonitrile/diethyl ether afforded red needles in 65% yield. *Anal.* Calc. for $C_{42}H_{72}N_2O_{12}Mo$: C, 56.5, H, 8.07; N, 3.14. Found: C, 56.4; H, 8.20; N, 3.21%. IR (KBr pellets, cm^{-1}): 2965(m), 2880(m), 1745(m), 1720(w), 1645(s), 1505(vs), 1415(s), 1370(m), 1265(w), 1070(m), 945(m), 912(m), 803(m), 744(w), 628(m), 580(m), 550(w), 495(m), 290(m).

Preparation of $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_4(C_5O_5)_2]$

Addition of hydrazine (1 ml) to a solution of $[(n\text{-}C_4H_9)_4N]_2[MoO_2(C_5H_5)_2]$ (4.46 g, 5 mmol) in me-

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thylene chloride (100 ml) yields a dark brown solution. Addition of diethyl ether and standing for three weeks results in orange crystals in 25% yield. *Anal.* Calc. for $C_{42}H_{72}N_2O_{14}Mo_2$: C, 49.4; H, 7.06; N, 2.75. Found: C, 49.2; H, 6.87; N, 2.87%. IR (KBr pellet, cm^{-1}): 2960(m), 2875(m), 1740(m), 1725(w), 1645(s), 1500(vs), 1420(s), 1355(m), 1250(w), 1070(m), 965(m), 800(m), 735(s), 630(m), 570(m), 490(m), 285(m).

X-ray structure determination

Full details of the crystal data and data collection and refinement procedures are given in Table 1. Full details of the crystallographic methodologies may be found in ref. 22. Atomic coordinates are given in Table 2.

In no instance was an extinction correction applied to the data. Idealized hydrogen atom positions were used throughout the analysis, with the C–H and N–H distances set a 0.96 and 0.94 Å, respectively. All non-hydrogen atoms of the anion were refined anisotropically, as were the N atoms of the cations. All other atoms were treated isotropically.

Results and discussion

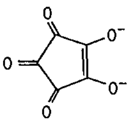
The oxocarbon species, squaric acid and rhodizonic acid, have been shown to react with polyoxomolybdate anions to give a variety of polynuclear species. In contrast, reaction of $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_7]$ with barium croconate yields a mononuclear species $[(n\text{-}C_4H_9)_4N]_2[MoO_2(C_5O_5)_2]$ (**4**). The infrared spectrum of **4** exhibits bands in the 1640 to 1745 cm^{-1} range characteristic of $\nu(C{=}C)$ and $\nu(C{=}O)$ of the coordinated croconate group. The bands at 945 and 912 cm^{-1} are assigned to ν_s and ν_{as}, respectively, of the *cis*-dioxomolybdate unit.

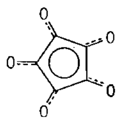
Reduction of **4** by hydrazine yields the Mo(V) binuclear species $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_4(C_5O_5)_2]$ (**5**) as a microcrystalline orange precipitate. The infrared spectrum of **5** exhibits characteristic croconate bands between 1650 and 1750 cm^{-1} and bands at 965 and 945 cm^{-1} assigned to $\nu_s(Mo{=}O)$ and $\nu_{as}(Mo{=}O)$, respectively. The strong band at 735 cm^{-1} confirms the presence of the MoO_2Mo units [23]. Although chemical reduction of **4** proceeds smoothly, the electrochemistry of **4** exhibits only an ill-defined reduction at potentials more negative than −1.50 V (Pt working electrode, ferrocene/ferrocenium reference, 2 mM complex in CH_2Cl_2). This result is not surprising since reduction of the $[MoO_2]^{2+}$ core requires population of an antibonding orbital and consequently considerable structural reorganization [24]. Since the reduced species is stabilized by formation of the binuclear $[Mo_2O_4]^{2+}$ core and displacement of croconate anion, irreversible electrochemistry is not unanticipated.

$$2[MoO_2(C_5O_5)_2]^{2-} + 2e^- \longrightarrow [Mo_2O_4(C_5O_5)_2]^{2-} + 2C_5O_5{}^{2-}$$

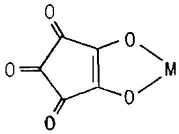
The structure of **4** consists of discrete $(n\text{-}C_4H_9)_4N^+$ cations and $[MoO_2(C_5O_5)_2]^{2-}$ anions, whose structure is illustrated in Fig. 1. The anion exhibits the characteristic distorted octahedral geometry associated with the *cis*-dioxomolybdate(VI) core. The Mo–oxo distances of 1.684(7) and 1.710(7) Å, given in Table 3, and the O1–Mo–O2 angle of 105.6(4)° are unexceptional. The significant *trans* influence of the strongly π-bonded oxo groups is apparent in the Mo–O3 and Mo–O8 distances of 2.246(6) and 2.251(6) Å, respectively, as compared to the Mo–O4 and Mo–O9 distances of 2.019(6) and 2.044(6) Å, respectively.

The croconate ligands assume the 1,2-bidentate chelating or η^2-geometry. Other structurally characterized metal–croconate complexes exhibit 1,2,4-coordination of the croconate groups, as a consequence of bonding to a second metal site through the oxygen donor at position 4 in addition to the 1,2-chelation to the primary metal site [25, 26]. Although squarate does not exhibit the η^2-coordination mode, the relief of strain consequent to ring expansion to the five-membered croconate ring





allows the 1,2-chelate or η^2-coordination geometry. The croconate geometry is consistent with the localized structure (**6**). The bond distances may be compared to those of the free croconate anion which exhibits extensive delocalization with equivalent C–C and C–O distances of 1.45 and 1.26 Å, respectively [27].



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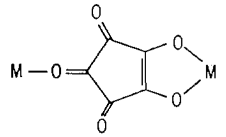

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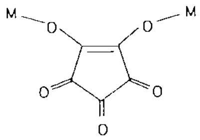

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Although the coordination chemistry of the croconate anion has not been as extensively studied as that of squarate, a number of thermal investigations of croconate complexes [28, 29] have been described,

TABLE 1. Summary of experimental details for the X-ray diffraction study of $[(n\text{-}C_4H_9)_4N]_2[MoO_2(C_5O_5)_2]$

Crystal parameters at 296 K[a]	
a (Å)	36.502(11)
b (Å)	14.681(4)
c (Å)	18.109(5)
α (°)	90.00
β (°)	93.84
γ (°)	90.00
V (Å^3)	9682.5(15)
Space group	$C2/c$
Z	8
D_{calc} (g cm^{-3})	1.22
Measurement of intensity data	
Crystal shape and color	red needle
Crystal dimensions (mm)	$0.28 \times 0.45 \times 0.32$
Instrument	Nicolet R3m diffractometer
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Scan mode	Coupled θ(crystal)–2θ(counter)
Scan rate (°/min)	2–30
Scan range (°)	$2.0° < 2\theta \leqslant 50°$
Scan length	from $[2\theta(K\alpha_1) - 1.0]°$ to $[2\theta(K\alpha_2) + 1.0]°$
Background measurement	stationary crystal, stationary counter, at the beginning and at the end of each 2θ scan, each for half the time taken for the scan
Standards	3 collected every 197
No. reflections collected	6909
No. reflections used in solution $F_o \geqslant 6\sigma(F_o)$	3593
Reduction of intensity data and summary of structure solution and refinement[b]: data corrected for background, attenuators, Lorentz and polarization effects in the usual fashion	
Absorption coefficient (cm^{-1})	3.20
Absorption correction (not applied)	
T_{max}/T_{min}	1.10
Structure solution	Patterson synthesis yielded the heavy atom position; all remaining non-hydrogen atoms were located via standard Fourier techniques
Atom scattering factors[c]	neutral atomic scattering factors were used throughout the analysis
Anomalous dispersion[d]	applied to all non-hydrogen atoms
Final discrepancy factor[e]	
R	0.0693
R_w	0.0744
Goodness of fit[f]	1.95

[a] From a least-squares fitting of the setting angle of 25 reflections. [b] All calculations were performed on a Micro-Vax II computer using local versions of the Nicolet SHELXTL interactive crystallographic software package as described in ref. 19. [c] Ref. 20. [d] Ref. 21. [e] $R = \Sigma[|F_o| - |F_c|/\Sigma|F_o|]$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\delta^2(F_o + g^*(F_o))$; $g = 0.001$. [f] $GOF = [\Sigma w(|F_o| - F_c|)^2/(NO - NV)]^{1/2}$ where NO is the number of observations and NV is the number of variables.

as well as studies of ligation to transition metal centers [22, 23, 30–33]. Although the 1,2,4-coordination mode is the most commonly adopted, the 1,2-bridging geometry (**8**) has been invoked, as well as the 1,2-η^2-chelating mode [31]. The structure of **4** provides confirmation of the latter ligating mode. The observation of exclusively 1,2-η^2-chelation in a complex with the $[MoO_2]^{2+}$ core is not unexpected since distorted octahedral geometry, wherein the coordination requirements of the Mo(VI) center are fully satisfied, is the predominant structural type for this core with oxygen donor ligands.

Supplementary material

Tables of bond lengths and angles, anisotropic temperature factors, calculated hydrogen atom positions and structure factors can be obtained upon request from J.Z.

Acknowledgement

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TABLE 2. Atomic coordinates (×10^4) for $[(n\text{-}C_4H_9)_4N]_2[MoO_2(C_5O_5)_2]$

	x	y	z
Mo(1)	819(1)	2005(1)	8585(1)
O(1)	391(2)	2098(5)	8185(4)
O(2)	784(2)	1283(5)	9318(4)
O(3)	1434(2)	2006(5)	8764(3)
O(4)	981(2)	1161(4)	7788(3)
O(5)	1405(3)	−55(6)	6785(5)
O(6)	2187(3)	212(8)	7277(6)
O(7)	2235(3)	1530(7)	8497(5)
O(8)	1002(2)	3102(5)	7823(3)
O(9)	862(2)	3131(5)	9249(3)
O(10)	951(2)	5029(5)	9866(5)
O(11)	1151(3)	6183(6)	8619(5)
O(12)	1214(3)	5008(6)	7315(5)
C(1)	1573(3)	1483(7)	8277(5)
C(2)	1332(3)	1030(7)	7774(5)
C(3)	1527(4)	431(8)	7264(6)
C(4)	1926(4)	573(9)	7514(7)
C(5)	1960(4)	1261(8)	8170(7)
C(6)	1025(3)	3854(8)	8175(6)
C(7)	950(3)	3881(7)	8920(6)
C(8)	992(3)	4776(8)	9230(7)
C(9)	1104(3)	5385(9)	8606(7)
C(10)	1128(3)	4773(7)	7902(8)
N(1)	1637(2)	2554(5)	1117(4)
N(2)	787(3)	2344(6)	5626(5)
C(11)	1536(2)	1728(6)	652(5)
C(12)	1844(3)	1126(6)	413(5)
C(13)	1700(3)	242(7)	66(6)
C(14)	1992(3)	−380(8)	−150(7)
C(15)	1927(3)	3109(7)	759(5)
C(16)	1819(3)	3477(7)	−1(5)
C(17)	2143(3)	3817(8)	−368(6)
C(18)	2063(3)	4146(9)	−1141(7)
C(19)	1299(3)	3128(6)	1191(5)
C(20)	1006(3)	2712(8)	1615(6)
C(21)	652(4)	3217(10)	1468(8)
C(22)	350(7)	2883(17)	1787(14)
C(23)	1801(3)	2227(7)	1863(5)
C(24)	1898(3)	2964(7)	2427(6)
C(25)	2069(4)	2485(10)	3155(7)
C(26)	2164(4)	3088(10)	3792(8)
C(27)	541(4)	3173(10)	5618(8)
C(28)	423(5)	3515(13)	6243(10)
C(29)	117(5)	4373(14)	6111(11)
C(30)	15(8)	4528(21)	6832(14)
C(31)	1146(3)	2478(8)	6055(7)
C(32)	1373(4)	3235(9)	5828(8)
C(33)	1739(4)	3242(10)	6333(9)
C(34)	1960(5)	4050(13)	6190(10)
C(35)	831(4)	2174(10)	4808(7)
C(36)	1038(6)	1530(14)	4602(10)
C(37)	1038(6)	1304(16)	3701(10)
C(38)	783(6)	1128(16)	3395(11)
C(39)	614(4)	1531(9)	5988(7)
C(40)	306(5)	1213(13)	5727(10)
C(41)	177(6)	292(14)	6158(12)
C(42)	350(6)	−322(14)	6102(13)

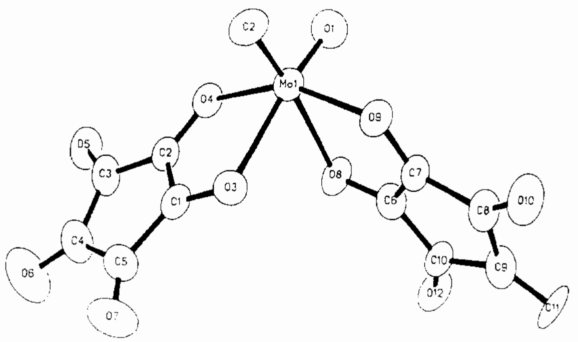

Fig. 1. ORTEP view of $[MoO_2(C_5O_5)_2]^{2-}$, showing the atom-labelling scheme.

TABLE 3. Selected bond lengths (Å) and angles (°) for $[(n\text{-}C_4H_9)_4N]_2[MoO_2(C_5O_5)_2]$

Mo–O1	1.684(7)	O3–C1	1.298(12)
Mo–O2	1.710(7)	O4–C2	1.298(14)
Mo–O3	2.246(6)	O5–C3	1.188(14)
Mo–O4	2.019(6)	O6–C4	1.194(18)
Mo–O8	2.251(7)	O7–C5	1.197(15)
Mo–O9	2.044(6)	C1–C2	1.395(14)
		C2–C3	1.490(16)
		C3–C4	1.510(20)
		C4–C5	1.558(17)
		C5–C1	1.474(17)
		O8–C6	1.275(13)
		O9–C7	1.303(12)
		O10–C8	1.230(15)
		O11–C9	1.184(15)
		O12–C10	1.179(16)
		C6–C7	1.395(15)
		C7–C8	1.433(15)
		C8–C9	1.520(17)
		C9–C10	1.567(18)
		C10–C6	1.494(16)
O1–Mo–O2	105.6(4)	Mo–O3–C1	109.6(6)
O1–Mo–O3	162.1(3)	Mo–O4–C2	116.2(6)
O1–Mo–O4	92.8(3)	Mo–O8–C6	109.0(6)
O1–Mo–O8	88.9(3)	Mo–O9–C7	115.2(6)
O1–Mo–O9	102.7(3)	C2–C1–C5	112.2(9)
O2–Mo–O3	90.9(3)		
O2–Mo–O4	102.4(3)	C1–C2–C3	112.2(10)
O2–Mo–O8	163.8(3)	C2–C3–C4	103.0(10)
O2–Mo–O9	93.0(3)		
O3–Mo–O4	76.5(3)	C3–C4–C5	110.1(11)
O3–Mo–O8	75.8(2)	C1–C5–C4	102.5(10)
O3–Mo–O9	83.0(3)	C7–C6–C10	111.4(10)
O4–Mo–O8	83.6(2)	C6–C7–C8	112.4(10)
O4–Mo–O9	154.4(3)	C7–C8–C9	106.0(10)
O8–Mo–O9	76.6(2)	C8–C9–C10	107.4(10)
		C6–C10–C9	102.7(10)

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