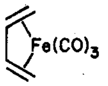
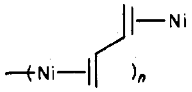
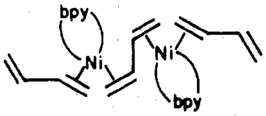
into its η^4 counterpart



(iii) the proposed polymeric nature of the gray product formed from Ni/butadiene at 77 K, which is supposed to contain



repeat units,[8] (iv) the η^2-C_4H_6 bonding mode for the butadiene units in the complex[12]



(v) η^2 bridging in $K_2[(\eta^2\text{-}\mu\text{-}C_4H_6)PtCl_3]_2$,[14a] and (vi) η^2 monodendate bonding for *s-trans*-butadiene in $Pt(PPh_3)_2(\eta^2\text{-}C_4H_6)$[15] and $[PtCl_2(\eta^2\text{-}C_4H_6)]_2$.[16]

In summary, it would appear that the insensitivity of binary nickel–olefin optical spectra to olefin substituents but sensitivity to metal nuclearity may well prove to be a general tool for the characterization of such species, with respect to olefin stoichiometry and mode of olefin coordination. The extension of the work to nickel vapor–polyolefin polymer systems incorporating unsaturated moieties is an obvious next step and one that is already under way in these laboratories.[17]

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[17] C G. Francis, M. Andrews, and G. A. Ozin, work in preparation.

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Synthesis and Characterization of the Organobismuthomolybdates $[(C_6H_5)_3Bi(MoO_4)_2]^{2-}$ and $[(C_6H_5)_3Bi(MoO_4)]_x$

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No heteropolymolybdates containing tetrahedrally coordinated Mo^{VI} are known, a surprising situation since several isopolymolybdates including $Mo_2O_7^{2-}$,[2] $Mo_{10}O_{34}^{8-}$,[3] and α-$Mo_8O_{26}^{4-}$[4] have been shown to contain tetrahedral Mo^{VI}. Due to the basicity and coordinative unsaturation of MoO_4^{2-}, heteropolyanions containing this unit might be expected to display types of reactivity not observed for complexes containing only octahedrally coordinated Mo^{VI}. We have therefore investigated the reactivity of MoO_4^{2-} toward $(C_6H_5)_3BiBr_2$, hoping to obtain not only simple substitution products but also organobismuth(III) reductive elimination products. The isolation of the $[(C_6H_5)_3Bi(MoO_4)_2]^{2-}$ anion and polymeric $[(C_6H_5)_3Bi(MoO_4)]_x$ are reported here. Although attempts to obtain well-characterized reductive elimination products have thus far failed, in the course of such attempts we have discovered a reaction between MoO_4^{2-} and CH_2Cl_2 which results in formation of the $CH_2Mo_4O_{15}H^{3-}$ anion.

Experimental Section

$(C_6H_5)_3BiBr_2$ was prepared according to a literature procedure[5] using CCl_4 as solvent and was recrystallized by slow addition of C_2H_5OH to a saturated $CHCl_3$ solution. $(C_6H_5)_3Bi$ (Eastman Kodak), MoO_3 (Fisher), and 1 M $(n\text{-}C_4H_9)_4NOH$ in CH_3OH (Eastman Kodak) were used without further purification. The solvents CH_2Cl_2, $(C_2H_5)_2O$, $C_6H_5CH_3$, and $(CH_3)_2CO$, all ACS Certified from commercial sources, were not purified. $CHCl_3$ (Fisher, ACS Certified) was distilled over P_2O_5 for ^{17}O NMR measurements only. CH_3CN (Aldrich, 99%) was distilled over P_2O_5 before use as a reaction solvent and was further purified by distillation over CaH_2 before use for conductivity and ^{17}O NMR measurements. Compounds **1** and **2** were enriched to 20 atom % ^{17}O for ^{17}O NMR studies by stirring overnight with enriched water in CH_3CN and $CH_3CN/CHCl_3$ (1:6, v/v), respectively. Enriched compounds were isolated and purified as described below for unenriched samples.

^1H NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer operating at 90 MHz. Proton-decoupled 25.03-MHz ^{13}C NMR spectra and 13.513-MHz ^{17}O NMR spectra were measured at 25 °C by using the pulse FT NMR technique on a Jeol PFT/PS-100 NMR spectrometer interfaced with a Nicolet 1080 data system. ^{17}O chemical shifts were measured relative to pure H_2O (δ 0.0) as described in ref 6b; ^{13}C chemical shifts were measured relative to the $CDCl_3$ solvent (δ 77.0). The conductance of **1** was measured in CH_3CN over a concentration range of 10^{-2}–10^{-4} equiv/L at 25.0 ± 1 °C with use of a Beckman RC-18A conductivity bridge. Elemental analyses and the molecular weight determination were performed by Galbraith Laboratories.

$[(n\text{-}C_4H_9)_4N]_2[(C_6H_5)_3Bi(MoO_4)_2]\cdot 3H_2O$ (1). Method A. A total of 1.30 g of MoO_3 (9.0 mmol) was stirred in 18 mL of 1 M $(n\text{-}C_4H_9)_4NOH$ (18 mmol) in CH_3OH for 6 h and filtered to remove a small amount of unreacted MoO_3. The filtrate was then evaporated under vacuum to a viscous oil containing $[(n\text{-}C_4H_9)_4N]_2MoO_4$. A solution of 2.70 g of $(C_6H_5)_3BiBr_2$ (4.5 mmol) in 20 mL of CH_2Cl_2 was added to this oil. After the resulting solution was stirred for 30 min, an excess of $(C_2H_5)_2O$ was added, and the resulting white precipitate was filtered off and dried in vacuo, 5.15 g (88% yield) of crude product was obtained. Colorless, needle-shaped crystals were grown from this crude product in 88% yield by dissolving it into a solution of 45 mL of CH_3CN in 72 mL of $(C_2H_5)_2O$ and cooling to 0 °C.

Method B. A total of 2.25 mmol of $[(n\text{-}C_4H_9)_4N]_2MoO_4$, prepared as described above for method A in 20 mL of CH_2Cl_2, was added to 1.35 g of $[(C_6H_5)_3Bi(MoO_4)]_x$ (2.25 mmol) and stirred for 30 min. After the solution was filtered, 2.65 g of crude product (91% yield) was isolated by following the procedures employed in method A.

Compound **1** is soluble in organic solvents such as CH_2Cl_2, $CHCl_3$, $(CH_3)_2CO$, CH_3CN, 1,2-$C_2H_4Cl_2$, and C_2H_5OH. Anal. Calcd for $C_{50}H_{93}N_2BiMo_2O_{11}$: C, 46.22; H, 7.21; N, 2.16; Bi, 16.08; Mo, 14.77. Found: C, 46.41; H, 7.35; N, 2.16; Bi, 15.91; Mo, 14.93. ^1H NMR in CD_2Cl_2 displays an *o*-C_6H_5 proton doublet at δ 8.4, a *m*- and *p*-C_6H_5 proton multiplet at δ 7.2–7.7, and an NCH_2 multiplet at δ 3.0–3.4 with relative intensities 5.8:9.2:16.0. ^{13}C NMR (δ, $CDCl_3$, ^1H decoupled): 156.3, 134.6, 130.4 (C_6H_5); 57.8, 23.4, 19.2, 13.2 ($CH_2CH_2CH_2CH_3$).

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$[(C_6H_5)_3Bi(MoO_4)]_x$ (2). This compound is light sensitive and must be prepared and handled in darkness to avoid decomposition to a $CHCl_3$ insoluble substance.

Method A. A solution of 3.46 mmol of $[(n\text{-}C_4H_4)_4N]_2MoO_4$ in 20 mL of CH_3CN, prepared as described above for compound **1**, was added to 2.08 g of $(C_6H_5)_3BiBr_2$ (3.46 mmol) and stirred rapidly for 1 h. The white precipitate which formed during this time period was filtered off, washed twice with 5 mL of CH_3CN, and dried in vacuo to yield 1.81 g (87% yield) of crude product. This material was purified by dissolving in $CHCl_3$, filtering, and precipitating with excess $(C_2H_5)_2O$.

Method B. An 82% yield of unpurified product is obtained from 0.80 g of $(C_6H_5)_3BiBr_2$ (1.33 mmol) and 1.72 g of **1** (1.32 mmol) in 20 mL of CH_3CN by following the same procedures employed in method A. Anal. Calcd for $C_{18}H_{15}BiMoO_4$: C, 36.02; H, 2.52; Bi, 34.82; Mo, 15.98. Found: C, 35.89; H, 2.44; Bi, 34.74; Mo, 15.80. The ^1H NMR spectrum in $CDCl_3$ displays only two broad unresolved multiplets at δ 7.2–7.5 and δ 7.7–8.0 with an intensity ratio of 2:3.2. ^{13}C NMR (δ, $CDCl_3$, ^1H decoupled): 154.5, 133.5, 131.5.

$[(n\text{-}C_4H_9)_4N]_3(CH_2Mo_4O_{15}H)$. Method A. An oil containing 6.94 mmol of $[(n\text{-}C_4H_9)_4N]_2MoO_4$, prepared as described above under method A for compound **1**, was dissolved in 10 mL of CH_2Cl_2 plus 7 mL of $C_6H_5CH_3$. The resulting solution was heated (without stirring) to 58 °C. After 4 h, during which a white precipitate was formed, the reaction mixture was cooled to room temperature, and excess ether was added to obtain additional precipitate. The precipitate then was filtered off, washed with acetone and ether, and dried under vacuum, yielding 2.1 g of product (88% yield), identified by IR spectroscopy.

Method B. One gram of **1** was dissolved in 10 mL of CH_2Cl_2 plus 8 mL of $C_6H_5CH_3$ and heated (without stirring) to 58 °C for 16 h. The clear solution was then cooled to room temperature, and excess $(C_2H_5)_2O$ (about 150 mL) was added to form an oil from which the supernatant ether layer was decanted. Addition of 5 mL of $(CH_3)_2CO$ to this oil, followed by shaking, yielded a white precipitate which was filtered off, washed with acetone and ether, and dried under vacuum. The 0.13 g of reaction product was identified as a mixture of α-$[(n\text{-}C_4H_9)_4N]_4(Mo_8O_{26})$ and $[(n\text{-}C_4H_9)_4N]_3(CH_2Mo_4O_{15}H)$ by IR spectroscopy. These components could be separated by adding CH_2Cl_2 since the former is only slightly soluble and the latter is very soluble. The yield and purity of product could not be significantly enhanced since $[(n\text{-}C_4H_9)_4N]_3(CH_2Mo_4C_{15}H)$ decomposes to α-$[(n\text{-}C_4H_9)_4N]_4(Mo_8O_{26})$ under the reaction conditions.

Results and Discussion

$[(n\text{-}C_4H_9)_4N]_2[(C_6H_5)_3Bi(MoO_4)_2]\cdot 3H_2O$ (**1**), prepared from either $(C_6H_5)_3BiBr_2$ and 2 equiv of $[(n\text{-}C_4H_9)_4N]_2(MoO_4)$ or $[(C_6H_5)_3Bi(MoO_4)]_x$ and $[(n\text{-}C_4H_9)_4N]_2(MoO_4)$, is a 2:1 electrolyte in CH_3CN according to conductivity measurements [$\Lambda_0 = 151$; $A = 680$ ($A_{calcd} = 686$)[7]]. The ^{17}O NMR spectrum of **1** shows only two resonances, at δ 659 and δ 267, in addition to the water resonance at δ −5. With a chemical shift value downfield from the free MoO_4^{2-} oxygen resonance (δ 532[8]) and upfield from the $Mo_2O_7^{2-}$ terminal oxygen resonance (δ 715[6b]), 11M50 δ 659 resonance can be assigned to the terminal trioxo group of a tetrahedral molybdate unit.[6] The δ 267 resonance has a chemical shift value typical for a bridging oxygen.[6] The ^{13}C NMR spectrum of **1** indicates only one type of phenyl group in the anion. These spectroscopic data support a structure involving trigonal-bipyramidal geometry at bismuth, with phenyl groups occupying equatorial sites and unidentate tetrahedral oxoanions occupying the axial sites. Axial oxygen ligands and equatorial phenyl groups of this type have been observed crystallographically in $[(C_6H_5)_3Bi(ClO_4)]_2O$.[9]

Reaction of compound **1** with one equivalent of $(C_6H_5)_3BiBr_2$ in CH_3CN yields $[(C_6H_5)_3Bi(MoO_4)]_x$ (**2**) as an amorphous precipitate. The same precipitate can also be prepared from equimolar amounts of $[(n\text{-}C_4H_9)_4N]_2MoO_4$ and $(C_6H_5)_3BiBr_2$ in CH_3CN. A molecular weight of 6700, determined by osmometry in $CHCl_3$, shows compound **2** to be polymeric. Only a single, very broad (600 Hz) resonance at δ 742 is observed in the ^{17}O NMR spectrum of **2**. The remaining resonance(s) are presumably too broad to be observed. The chemical shift value of the observed resonance, upfield relative to the monooxo terminal oxygens at tetrahedral molybdenum in α-$Mo_8O_{36}^{4-}$ (δ 775[6b]) and downfield relative to the trioxo terminal oxygens in $Mo_2O_7^{2-}$ (δ 715[6b]), can be assigned to dioxo terminal oxygens at tetrahedral molybdenum.[6] As with compound **1**, ^{13}C NMR spectra of **2** show only one type of phenyl group. We propose, therefore, a structure for **2** where $(C_6H_5)_3Bi^{2+}$ units are linked together by bridging MoO_4^{2-} groups such that each molybdenum is bonded tetrahedrally to two terminal oxygens and two Mo–O–Bi bridging oxygens and each bismuth is in a trigonal-bipyramidal environment with three equatorial phenyl groups and two axial molybdate oxygens. We emphasize, however, that this structure is only the simplest of many structures consistent with the experimental data available, especially since we have considered the structure to be stereochemically rigid.

At elevated temperatures, compound **1** reacts with CH_2Cl_2 to yield $[(n\text{-}C_4H_9)_4N]_3(CH_2Mo_4O_{15}H)$.[10] The $(C_6H_5)_3Bi(MoO_4)_2^{2-}$ reactant apparently serves only as a source of MoO_4^{2-}, however, since $[(n\text{-}C_4H_9)_4N]_2MoO_4$ reacts with CH_2Cl_2 under similar conditions to form the same product.

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Registry No. **2**, 74868-73-8; $[(n\text{-}C_4H_9)_4N]_2[(C_6H_5)_3Bi(MoO_4)_2]$, 74868-89-6; $[(n\text{-}C_4H_9)N]_3(CH_2Mo_4O_{15}H)$, 69701-02-6; $[(n\text{-}C_4H_9)_4N]_2MoO_4$, 74854-47-0; $(C_6H_5)_3BiBr_2$, 28719-55-3; CH_2Cl_2, 75-09-2.

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