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TRITHIOPEROXYBENZOATO(η^3-DITHIOBENZOATO)OXOMOLYBDENUM(IV), $MoO(S_3CPh)(\eta^3-S_2CPh)$: SYNTHESIS AND X-RAY MOLECULAR STRUCTURE

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The titled novel complex was obtained by the reaction of sodium molybdate(VI) dihydrate with diethylammonium dithiobenzoate in an acidic aqueous medium. An X-ray structure analysis of this complex has revealed the presence of trithioperoxybenzoato and η^3-dithiobenzoato ligands both coordinated to oxomolybdenum(IV).

Dithiolato ligands, such as dialkyldithiocarbamates,[1)] are known to react with sodium molybdate(VI) in the presence of reducing agents, giving bis(dithiolato)oxomolybdenum(IV) complexes. In the course of studies on oxomolybdenum complexes, we have found that the reaction of sodium molybdate(VI) dihydrate with diethylammonium dithiobenzoate in an acidic aqueous medium affords trithioperoxybenzoato(η^3-dithiobenzoato)oxomolybdenum(IV).

To an aqueous solution containing $Na_2MoO_4 \cdot 2H_2O$ (2.00 g, 8.26 mmol), $[(C_2H_5)_2NH_2][S_2CPh]$ (1.88 g, 8.35 mmol), and $NaOCOCH_3$ (2.04 g, 24.9 mmol) was added dropwise 20 cm^3 of hydrochloric acid (1 mol dm^{-3}) to give a yellow precipitate, which quickly turned brown. The precipitate was collected by filtration, washed with water and then with methanol, and dried *in vacuo*. The green solid obtained was dissolved in dichloromethane and chromatographed on an alumina column using dichloromethane as an eluent. The first violet eluate fraction was evaporated to dryness under reduced pressure. The product obtained was recrystallized from a mixture of dichloromethane and petroleum ether to give dark violet needles, which were identified as tetrakis(dithiobenzoato)-molybdenum(IV), $Mo(S_2CPh)_4$, on the basis of elemental analysis and of infrared and electronic spectra.[2)] The second yellow eluate fraction also was evaporated to dryness under reduced pressure. The product was recrystallized from acetone to yield orange plates (0.40 g, 0.89 mmol), mp 161-162°C. Anal. Calcd for $C_{14}H_{10}OS_5Mo$: C, 37.33; H, 2.24%. Found: C, 37.32; H, 2.25%.

The crystal and molecular structures of the orange complex have been determined by single-crystal X-ray analysis. Crystal data: Monoclinic, space group $P2_1/c$; $a = 15.614(2)$, $b = 8.441(1)$, $c = 13.125(2)$ Å, $\beta = 104.46(1)°$; $U = 1675.0(4)$ Å^3; D_m(flotation) = 1.76 g cm^{-3}, $Z = 4$, $D_x = 1.786$ g cm^{-3}. The intensity data were collected on an automatic diffractometer with graphite-monochromatized Mo-Kα radiation. The structure was solved by the standard heavy-atom method and refined by the block diagonal least-squares procedure. Anisotropic thermal vibrations were assumed for all the non-hydrogen atoms. All the hydrogen atoms were revealed from a difference Fourier map and refined isotropically. The conventional R value was 3.5% for 3767 independent reflections with $|F_0| > 3\sigma(F)$.

The crystal structure consists of four discrete molecules per unit cell. Figure illustrates

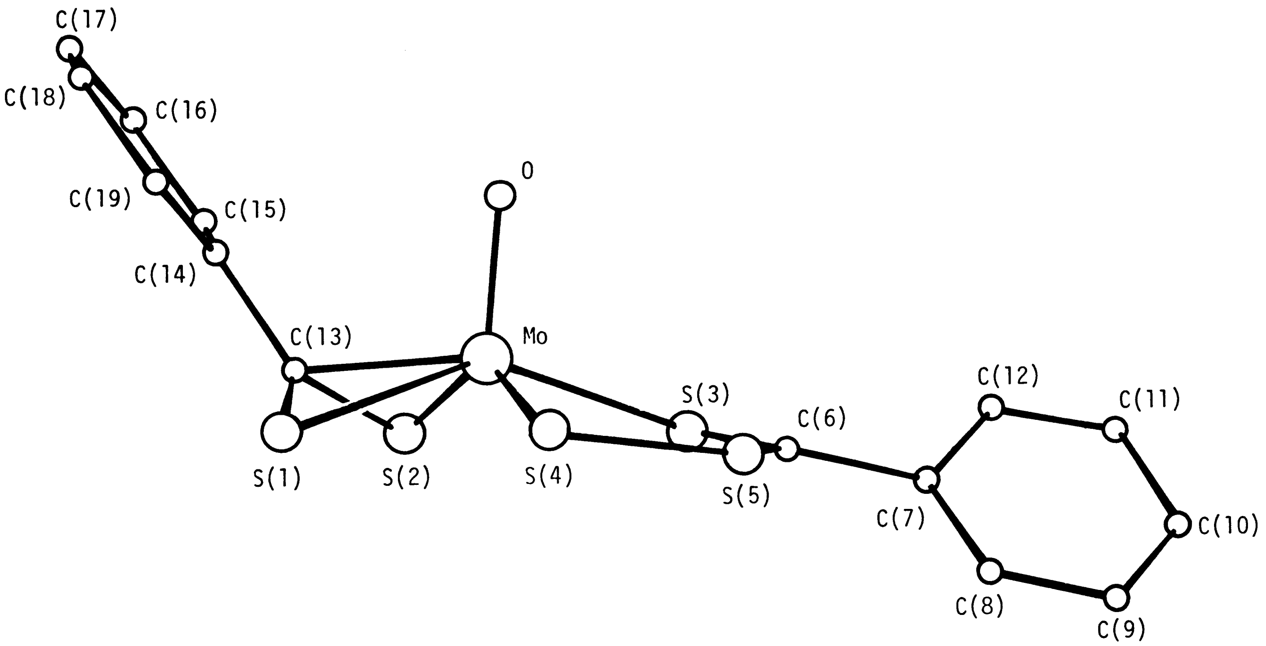

Figure. Molecular structure of $MoO(S_3CPh)(\eta^3-S_2Ph)$. Relevant bond lengths (in Å) and angles (in degrees) are: Mo-O, 1.671(2); Mo-S(1), 2.368(1); Mo-S(2), 2.362(1); Mo-S(3), 2.416(1); Mo-S(4), 2.376(1); Mo-C(13), 2.217(3); S(1)-C(13), 1.745(4); S(2)-C(13), 1.730(3); S(3)-C(6), 1.700(4); S(5)-C(6), 1.667(3); S(4)-S(5), 2.049(1); C(6)-C(7), 1.470(4); C(13)-C(14), 1.494(5); O-Mo-S(1), 113.98(8); O-Mo-S(2), 113.36(9); O-Mo-S(3), 104.82(7); O-Mo-S(4), 108.19(9); S(1)-Mo-S(2), 78.09(4); S(3)-Mo-S(4), 86.76(3); S(1)-C(13)-S(2), 118.1(2); Mo-S(3)-C(6), 109.1(1); Mo-S(4)-S(5), 107.94(4); S(4)-S(5)-C(6), 106.8(1); S(3)-C(6)-S(5), 125.2(2).

the molecular structure, which shows the presence of trithioperoxybenzoate coordinated to molybdenum. This is the first molybdenum complex of trithioperoxybenzoate, although zinc(II), nickel(II), palladium(II), and platinum(II) complexes involving trithioperoxyarylates have been reported.$^{3)}$ The S(1), S(2), S(3), and S(4) atoms form an approximate basal plane of the tetragonal pyramid around Mo; Mo and C(13) are placed 0.81 and 0.69 Å above the plane, respectively, and both C(6) and S(5) 0.27 Å below it. Thus, an approximate plane consisting of S(3), S(4), S(5), and C(6) makes a small angle to the basal plane. The phenyl ring of the trithioperoxybenzoato moiety is twisted by 48.4° from the basal plane and by 41.8° from the S(3)-S(4)-S(5)-C(6) plane.

The most characteristic feature on the molecular structure is a very short distance between Mo and C(13) (2.22(3) Å), suggesting the coordination of C(13) as well as S(1) and S(2) to Mo. Thus, the plane consisting of S(1), S(2), and C(13) makes an angle of 50.7° from the basal plane. A similar η^3-coordination of the CS_2 moiety has recently been reported for bis(isopropylthioxantato)-oxomolybdenum(IV) on the basis of X-ray analysis.$^{4)}$

References

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