

detected¹² we consider **4** an unlikely candidate. Furthermore, there appears to be no precedent for ring opening of such a bicyclic to a monocyclic cation. Finally, if **4** were the intermediate, the value of ρ for the cyclization might be expected to be larger than -3 . Thus, the dependence of para:ortho ratios on the leaving group,¹³ the second-order anchimeric assistance in a two-step scheme, the relatively low value of ρ , and the absence of products derived from an intermediate bicyclic cation are most easily accommodated by a mechanism involving the concerted formation of two rings.

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(12) For example, treatment of 0.40 mmol of substrate **1** ($R = R' = H$) with 3.45 mmol of zinc bromide in 100 ml of nitromethane for 16 min at -23° afforded, after chromatography, 0.12 mmol of starting cyclopentanol and 0.28 mmol of tetracyclic product **2** ($R = H$), accounting for 100% of the material. When the reaction period was extended to 23 min the yield of **2** ($R = H$) was essentially quantitative.

(13) The dependence of para-ortho ratios on the leaving group of **1** was also observed in the case of the zinc bromide catalyzed cyclization, although the effect was less pronounced than with stannic chloride.

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Trigonal Prismatic and Antiprismatic Coordination in an Isoelectronic Series of Tris(benzenedithiolato) Complexes

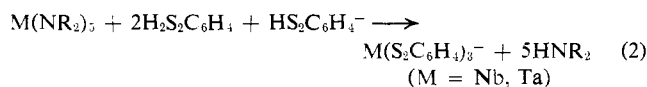
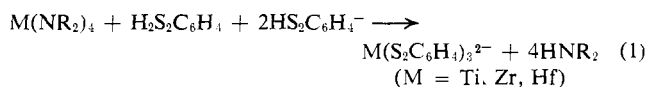
Sir:

The relative stabilities of the trigonal prismatic and antiprismatic coordination in tris(dithiolene) complexes of the transition metals have been the subject of considerable study.¹ The molecular orbital treatment of Gray, *et al.*,² has been particularly successful in explaining the physical properties of several trigonal prismatic complexes. In this energy level scheme, two types of molecular orbitals are important in stabilizing the trigonal prism. The first, $2a_1'$ using the notation of Gray, *et al.*, is the bonding combination of the ligand π_h orbitals with the metal d_{z^2} orbital. The second, $4e'$, is the bonding combinations of ligand π_v orbitals with the metal d_{xy} and $d_{x^2-y^2}$ orbitals. Information on the first of these factors has been investigated by studies of species where the antibonding combination $3a_1'$ is populated; *e.g.*, $\text{ReS}_6\text{C}_6(\text{C}_6\text{H}_5)_6$ with one electron in this orbital retains the trigonal prismatic structure³ while $\text{MoS}_6\text{C}_6(\text{CN})_6^{2-}$ with two electrons in this level has a structure intermediate between the prism and

antiprism.⁴ The irregular distortion⁵ of $\text{VS}_6\text{C}_6(\text{CN})_6^{2-}$ is not expected by the simple scheme, and reversals in the energy level ordering have been considered.⁶

The $4e'$ molecular orbitals are derived from metal and ligand orbitals which are close in energy and should be relatively sensitive to changes in the d orbital energies. We describe here the results of a crystallographic investigation of the structures of the isoelectronic series ZrL_3^{2-} , NbL_3^- , and MoL_3 (where L is the benzenedithiolate ligand) in which no changes may be ascribed to occupancy of the $3a_1'$ antibonding orbital. The observed changes should correspond to the changing d orbital energies and overall charge on the species. These two effects are linked and may not be separable.

The neutral molybdenum tris complex was prepared by the reaction of the pentachloride with the dithiol.² This type of reaction does not yield the corresponding zirconium and niobium anionic complexes. Therefore a new synthetic method was sought for these derivatives. Reaction of the transition metal amido complexes⁷ with stoichiometric quantities of the dithiol and its mono anion readily produces the desired trischelate complexes (eq 1 and 2). These reactions



afford all the advantages of an acid-base reaction: mild conditions, speed, absence of undesirable by-products, and consequentially good yield ($\sim 70\%$ after recrystallization). The complex anions were isolated and characterized as either their tetraalkylammonium (Ti, Zr, Hf) or tetraphenylarsonium (Nb, Ta) salts.

$\text{Mo}(\text{S}_2\text{C}_6\text{H}_4)_3$ crystallizes in the orthorhombic space group $Pnam$ with the unit cell dimensions $a = 16.093$ (3), $b = 10.177$ (1), $c = 11.906$ (2) Å, and four molecules per unit cell ($\rho_{\text{obsd}} = 1.74$, $\rho_{\text{calcd}} = 1.752$ g ml⁻¹). The structure (Figure 1) has been solved by conventional heavy-atom techniques using 1047 statistically reliable reflections measured using $\text{Cu K}\alpha$ radiation on a Picker FACS I diffractometer ($\sin \theta/\lambda_{\text{max}} = 0.575$) and has been refined by full-matrix least-squares techniques to give a conventional R value of 0.035. The molecules have the expected trigonal prismatic structure (approximate symmetry C_{3h}) with the crystallographic mirror plane being coincident with the molecular σ_h plane.

The tetraphenylarsonium salt of tris(benzenedithiolato)niobium crystallizes in the monoclinic system with space group $P2_1/n$, unit cell dimensions $a = 22.983$ (7) Å, $b = 12.747$ (4) Å, $c = 13.150$ (3) Å, $\beta = 92.09$ (2°), and four formula units per unit cell ($\rho_{\text{obsd}} = 1.52$, $\rho_{\text{calcd}} = 1.540$ g ml⁻¹). The structure has been solved using 3604 statistically reliable reflections and has been refined to a value of 0.049. Experimental conditions and procedures were essentially as for the molybdenum complex. The structure of the anion is trigonal prismatic with the longest yet observed sulfur-sulfur con-

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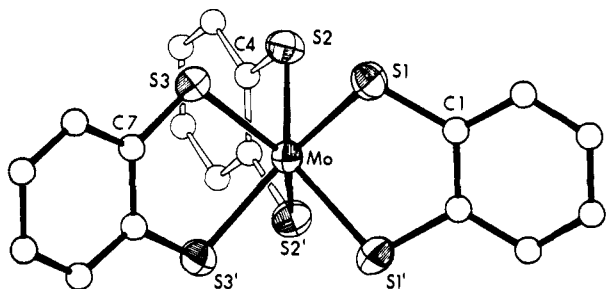
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(3) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **5**, 411 (1966).

Table IV

Complex	M-S, Å	S-C, Å	S···S, Å (intraligand)	S···S, Å (interligand)	Dihedral angles MS ₂ -S ₂ C ₆ (deg)
Mo(S ₂ C ₆ H ₄) ₃	2.367 (2)	1.726 (6)	3.110 (2)	3.091 (3)	13, 21, 30
Nb(S ₂ C ₆ H ₄) ₃ ⁻	2.441 (2)	1.743 (8)	3.150 (3)	3.232 (3)	22, 23, 23
Zr(S ₂ C ₆ H ₄) ₃ ²⁻	2.544 (2)	1.762 (10)	3.264 (5)	3.586 (5)	4, 0, 5

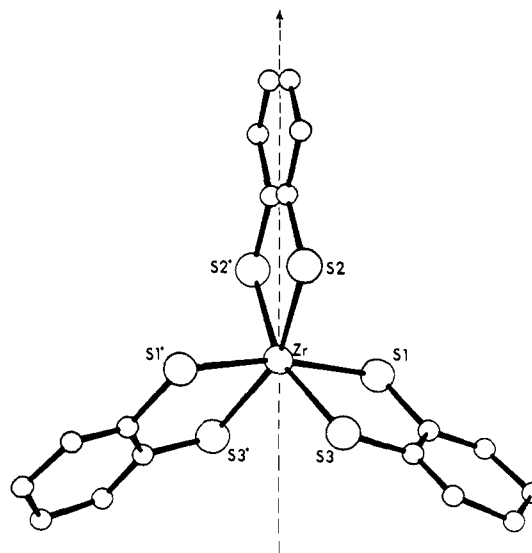
Figure 1. A perspective view of Mo(S₂C₆H₄)₃.

tacts for the trigonal prismatic structure and a marked difference between the inter- and intraligand distances.

The structure of tris(benzenedithiolato)zirconium dianion was determined for the tetramethylammonium salt which crystallizes in the orthorhombic space group *P*2₁2₁2, unit cell dimensions *a* = 9.931 (2), *b* = 14.368 (2), *c* = 11.098 (2) Å, and two formula units per unit cell ($\rho_{\text{obsd}} = 1.38$, $\rho_{\text{calcd}} = 1.381 \text{ g ml}^{-1}$). A preliminary set of significant reflections was used and the model was refined to 0.050. The anions are situated on the crystallographic twofold and exhibit a geometry intermediate between the trigonal prism and antiprismatic limits (Figure 2), although it is closer to the latter. Additional data are being collected for the zirconium complex to improve the precision of the structure. Fractional coordinates for all three structures are given⁸ in Tables I, II, and III.

The three structures demonstrate smooth increases in M-S and S-C distances (Table IV) in going from molybdenum to zirconium. The increase in S-C distances indicates an increase in the importance of the dithiolato formulation for the ligand. The central MS₆ units have approximate symmetry *D*_{3h} (Mo and Nb) and *D*₃ (Zr), and any deviations from these idealized symmetries arise probably due to intermolecular forces rather than intramolecular effects. The change in structure of this MS₆ unit in going from niobium to zirconium appears drastic, yet even the zirconium structure is closer to the trigonal prismatic structure than simple interligand repulsions arguments⁹ would predict. However, the ZrL₃²⁻ structure is closer to the expected antiprismatic structure than MoL₃²⁻ even though the 3a₁' antibonding level should be populated in the latter complex. This difference seems to reflect the higher energy of the zirconium d orbitals compared with the molybdenum d orbitals. However, a certain amount of caution should be exercised in this comparison since different ligands are involved. One would expect the 4e' level to increase its ligand character as the d orbital energies increase, which is consistent with the trends observed in the ligand geometries for this series of complexes. However, as the d orbital energies

(8) See paragraph at end of paper regarding supplementary material.
(9) D. L. Kepert, *Inorg. Chem.*, **11**, 1561 (1972).

Figure 2. A perspective view of the dianion Zr(S₂C₆H₄)₃²⁻.

increase so do their M-S distances increase; thus the S₆ coordination sphere expands and there is a reduction in the interligand bonding. Clearly the system involves several subtle and correlated effects.

The natural extension of the structural work is the determination of the geometry of the anions TiL₃²⁻ and TaL₃²⁻ where spectroscopic and X-ray powder diffraction data indicate marked differences from the structures of ZrL₃²⁻ and NbL₃²⁻, respectively.

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Supplementary Material Available. Tables I-III, atom coordinates for Mo(S₂C₆H₄)₃, [(C₆H₅)₄As][Nb(S₂C₆H₄)₃], and [(CH₃)₄N]₂[Zn(S₂C₆H₄)₃], will appear following these pages in the microfiche edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-73-7504.

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Relativistic Changes Accompanying Molecular Formation

Sir:

Since virtually all quantum mechanical calculations of molecular dissociation energies utilize the nonrela-