In order to study the inversion of a secondary amine in which the hydrogen is replaced by a deuterium, II was prepared by equilibration of I in D_2O, followed by salting out with NaOD, distillation from solid NaOD, and subsequent storage over solid NaOD. Compound II showed the same n.m.r. spectrum at room temperature (in CCl_4) as I, but the coalescence of the two resonance lines occurred only at 68°. Using the same two alternative methods of calculation as in the case of I, the activation energy of inversion was found 14.3 (from Figure 2, II) and 15.0 kcal./mole, respectively. These results are in agreement with the expected greater inertia of an N–D bond in its vibration through the plane of the ring, due to the greater mass of the deuterium.

Acknowledgment. The authors are grateful to Dr. A. L. VanGeet of the Chemistry Department for his helpfulness in connection with the low-temperature n.m.r. measurements.

Thomas J. Bardos, Csaba Szantay, C. Krishna Navada
Department of Medicinal Chemistry, School of Pharmacy
State University of New York at Buffalo, Buffalo, New York
Received August 30, 1965

The Crystal and Molecular Structure of $MoS_6C_6H_6$

Sir:

Recently[1-3] the first members of a class of neutral and charged transition metal complexes $M(S_2C_2H_2)_n^{-z}$ ($n = 2$ or 3, $z = 0, 1, 2$) of the hitherto unknown ligand dithioglyoxal have been reported, which are the important basic members of a large family of metal complexes of α-dithiodiketonic and of related bidentate sulfur donor ligands. The neutral tris complexes[4] are of particular interest since the recent X-ray analysis[5] of $Re(S_2C_2Ph_2)_3$[4a] revealed an unexpected prismatic structure. In addition it was concluded[5] from X-ray powder patterns that $Re(S_2C_2Ph_2)_3$ is isomorphous with the tungsten compound, but apparently not with the analogous and mutually isomorphous V, Cr, and Mo complexes. Independently, we have also observed that the phenyl substituted V, Cr, and Mo complexes are not isomorphous with the Re compound, but we also find the tungsten compound to be isomorphous with the latter group of compounds, while distinctly different from the Re complex.[6] Although there exists supporting evidence[5,7] suggesting prismatic structures for the majority of the tris complexes, a rigorous proof is necessary, especially since the X-ray powder patterns of the isomorphous complexes $MoS_6C_6H_6$ and $WS_6C_6H_6$ were also found to be *definitely different* from those of $ReS_6C_6H_6$.[8] In the present communication we report the results of an X-ray structural analysis of the unsubstituted molybdenum complex,[3] $MoS_6C_6H_6$. In addition to the reasons stated above, the structure of this complex is interesting as it represents the first example of a compound containing dithioglyoxal units.

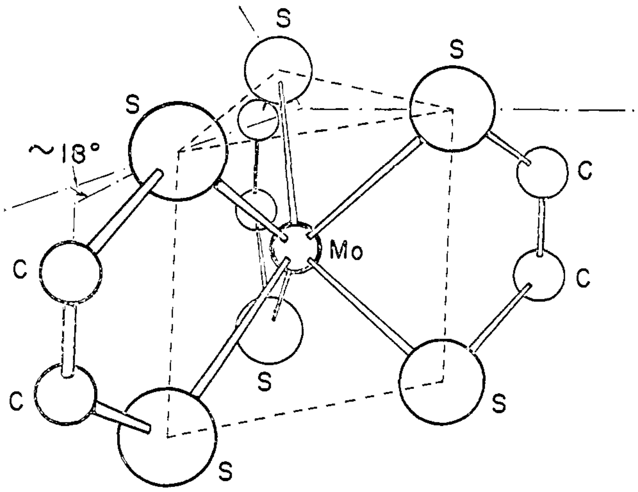

Figure 1. Schematic drawing of $[(HCS)_2]_3Mo$.

Limited three-dimensional data ($hk0$)–($hk3$) (layers of Weissenberg) plus ($h0l$) precession data were taken at −157° with Zr-filtered Mo radiation. A spherical crystal was used. The unit cell is hexagonal: $a = 7.632$, $c = 11.53$ Å., $Z = 2$, space group $P6_{3/m}$. The structure was solved using two-dimensional Patterson projections to locate the Mo, S, and C atoms. The refinement was carried out by least squares using the three-dimensional data. The Mo atoms are at the special positions ($^2/_3$, $^1/_3$, $^1/_4$) and ($^1/_3$, $^2/_3$, $^3/_4$), and the S and C atoms in a trigonal prismatic arrangement (Figure 1) around the Mo atoms, with symmetry C_{3h}. The carbon atoms are not in the plane passing through the Mo and S atoms but deviate 18° from this plane. The Mo–S distance is 2.33 Å. (±0.02), in good agreement with the value found in MoS_2, which also has trigonal prismatic coordination.[9] The S–C distance is 1.70 (±0.03) and the C–C 1.34 Å. (±0.04). The S–Mo–S angle is 82.5° and the S···S distance within the ligands is 3.10 Å. The distance between adjacent sulfur atoms related by the threefold axes is 3.11 Å. The molecules are relatively close-packed; in fact, the distance C–H···S between adjacent molecules is less than the sum of the van der Waals radii. The isotropic temperature factors are all quite low and of reasonable magnitude; the R factor at present is 0.11 and further refinement with more extensive data is in progress. With the exception of the deviation of the C atoms from the S–M–S plane, the bond distances and angles are in good agreement with those found by Eisenberg and Ibers for $Re(S_2C_2Ph_2)_3$, albeit this molecule has D_{3h} symmetry.

---

(1) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965).

(2) H. Hoyer and W. Schroth, *Chem. Ind.* (London), 652 (1965).

(3) G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *ibid.*, 1464 (1965).

(4) (a) G. N. Schrauzer, H. W. Finck, and V. P. Mayweg, *Angew. Chem.*, **76**, 715 (1964); *Angew Chem. Intern. Ed., Engl.*, **3**, 639 (1964); (b) J. H. Waters, R. Williams, H. B. Gray, G. N. Schrauzer, and H. W. Finck, *J. Am. Chem. Soc.*, **86**, 4198 (1964); (c) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **4**, 55 (1965); (d) R. B. King, *ibid.*, **2**, 641 (1963).

(5) R. Eisenberg and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 3776 (1965), and private communication prior to publication.

(6) The fact that the complexes of Cr, Mo, and W (with $S_2C_2Ph_2$ ligands) are isomorphous has been observed previously: G. N. Schrauzer, H. W. Finck, and V. P. Mayweg, *Z. Naturforsch.*, **19b**, 1080 (1964).

(7) E. I. Stiefel and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 4012 (1965).

(8) Note Added in Proof. In the meantime we have also obtained well-resolved X-ray powder diagrams of $VS_6C_6H_6$, $RuS_6C_6Ph_6$, and $OsS_6C_6Ph_6$. Tris(dithioglyoxal)vanadium is not isomorphous with the Mo, W, and Re compounds. The phenyl-substituted complexes of Ru and Os both gave different powder patterns, not identical with those of the V, Cr, Mo, W, and Re compounds.

(9) R. Dickinson and L. Pauling, *J. Am. Chem. Soc.*, **45**, 1466 (1923).

The C–S distance of 1.70 Å. is close to the mean of the values 1.62–1.75 Å. found in the rhenium complex.[4] We consider the geometry of the dithioglyoxal ligands in $MoS_6C_6H_6$ as the ultimate result of the accumulation of negative charge in the ligands. In agreement with general ideas of the bonding in complexes of this type outlined previously,[3] it must be pointed out that in C_{3h} as well as D_{3h} symmetry several of the σ- and π-bonding interactions fall into the same irreducible representations. The complexes are, therefore, three-dimensionally delocalized. Owing to the presence of low-lying π molecular orbitals in the isolated dithioglyoxal ligands, the highest occupied MO's in the complex, which belong to the symmetry E′, are localized both on the metal and the ligands but have predominantly ligand character. The occupation of this orbital will thus cause the ligands to resemble more closely dithiolato dianions; consequently, the C═S bond lengths are found similar to those in thiophene (observed[10] 1.71$_8$ Å.), while the C–C bond distances appear to be equal to conventional double bonds. The significant ligand character of the highest-occupied E′-type MO may, in addition, force the sulfur atoms into a state between sp^2 and sp^3 hybridization, which could receive additional stabilization through intermolecular packing effects. In the infrared spectrum (in KBr), C═C and C═S stretching vibrations are observed at 1401 and 1121 cm.$^{-1}$ and 857 cm.$^{-1}$, indicating a significant perturbation of these bonds; the C–H stretch appears in the expected olefinic region (3033 cm.$^{-1}$, in KBr). With this new interpretation of the bonding in these complexes it becomes also possible to assign a formal oxidation number to the central metal atoms. In the case of group VI transition metal complexes, the E′-type MO is fully occupied, leading to the oxidation number of +4. In view of the covalent nature of bonding in these compounds, this number has of course only formal significance. Full details of this theoretical evaluation will be presented in an extensive publication.

(10) B. Bak, D. Christensen, J. Rastrup-Andersen, and E. Tannenbaum, *J. Chem. Phys.*, **25**, 892 (1956).

A. E. Smith
Shell Development Company
Emeryville, California

G. N. Schrauzer, V. P. Mayweg, W. Heinrich
Shell Development Company, Emeryville, California, and
The Institute of Inorganic Chemistry, The University
Munich, Germany
August 30, 1965

Kinetics of the Lithium–Ammonia–Ethanol Reduction of Benzene. A Fourth-Order Reaction[1]

Sir:

Reduction of benzene to 1,4-dihydrobenzene by alkali metal and alcohol in ammonia solution was first reported by Wooster in 1939.[2] Hypotheses for the mechanism of this reaction and analogous reductions of numerous other aromatic substrates have commonly involved either (A) stepwise addition of two electrons to the substrate, forming in turn a radical anion and a dianion, which picks up two protons, or (B) protonation of the intermediate radical anion to yield a radical which picks up the second electron and proton.[3] These hypotheses have been based almost exclusively on product analysis, *i.e.*, rationalizations of specific products from reduction of various substrates. This type of analysis gives little insight into the many possible details of A or B, or even into a choice between them. Kinetic analysis, which should give much better insight, has been little used, presumably because of general experimental difficulties with metal–ammonia solutions and because of complications arising from an omnipresent reaction of the alkali metals which competes with substrate reduction. This competing reaction is hydrogen evolution. Previous papers in this series on metal–ammonia solutions reported successful kinetic analyses of the hydrogen evolution reaction, from both alcohol[4] and ammonia itself,[1] and we now wish to report the kinetic analysis of reduction of benzene by lithium and ethanol (eq. 1).

$$C_6H_6 + 2Li + 2EtOH \longrightarrow 2EtOLi + C_6H_8 \tag{1}$$

Our results are quite different from those of the one previous kinetic analysis of this important reaction; in 1959 Krapcho and Bothner-By reported that the rate law for (1) is third order over-all, first order in each of the three reactants.[5] Our rate data on reduction 1 were gathered using the same basic experimental techniques as Krapcho and Bothner-By,[6] but our data plotted according to the linear form of their third-order rate law give smooth curves. At first it was thought this difficulty could be attributed simply to the competing hydrogen evolution,[9] which they ignored. By use of lithium (rather than the more reactive sodium and potassium) and carefully purified ammonia,[6] competition due to hydrogen evolution from the solvent can be ignored, but reaction of lithium and ethanol (2) can

$$2Li + 2EtOH \longrightarrow 2EtOLi + H_2 \tag{2}$$

still be competitive.[10] However, two far more funda-

[1] Paper V in the series Reactions of Metal–Ammonia Solutions. For paper IV see *J. Am. Chem. Soc.*, **85**, 3530 (1963).

[2] C. B. Wooster, U. S. Patent 2,182,242 (1939); *Chem. Abstr.*, **34**, 1993 (1940). *Cf.* also C. B. Wooster and K. L. Godfrey, *J. Am. Chem. Soc.*, **59**, 596 (1937).

(3) *Cf.* (a) A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950); **12**, 17 (1958); (b) H. Smith, "Organic Reactions in Liquid Ammonia," Interscience Publishers, Inc., New York, N. Y., 1963, pp. 237–279; (c) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, pp. 61–71; (d) A. Streitwieser," Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 425 ff.

(4) E. J. Kelly, H. V. Secor, C. W. Keenan, and J. F. Eastham, *J. Am. Chem. Soc.*, **84**, 3611 (1962).

(5) A. P. Krapcho and A. A. Bothner-By, *ibid.*, **81**, 3658 (1959).

(6) The only distinction of our techniques would appear to be in refinement. Immediately prior to use, anhydrous ammonia was distilled through BaO into our equipment, which could be used in such a manner as to prevent introduction of unwanted metallic[7] and gaseous[8] catalysts. This equipment allowed rapid mixing of homogeneous ammonia solutions of the reactants (to initiate reaction), was entirely vacuum jacketed, provided for temperature control through pressure control by an attached manostat, and was attached to a gas buret for collection of gaseous products. Liquid samples from the ammonia solutions, removed through the double wall reaction vessel, were quenched and analyzed in the manner of Krapcho and Bothner-By.[5]

(7) H. L. Dryden, Jr., G. M. Webber, and J. A. Cella, *J. Org. Chem.*, **26**, 3237 (1961).

(8) J. F. Eastham and D. R. Larkin, *J. Am. Chem. Soc.*, **81**, 3652 (1959).

(9) J. F. Eastham, C. W. Keenan, and H. V. Secor, *ibid.*, **81**, 6523 (1959).

(10) When benzene, lithium, and alcohol were mixed in stoichiometric ratio (1:2:2) and there was no lithium ethoxide initially present, only 12% of the metal went to form hydrogen,[9] but since most of this evolution (eq. 2) occurred during the first portion of reduction (eq. 1), its effect on metal and alcohol concentrations throughout the reduction cannot be ignored. However, the presence of significant initial lithium ethoxide so retards evolution 2 as to obviate it as competitor to the reduction.