

PdCl₂ to react in benzene according to Fischer's method.²

In a typical preparation, 1 g. of PdCl₂, 1.05 g. of freshly sublimed AlCl₃, and 0.5 g. of Al were suspended in 50 ml. of anhydrous benzene and boiled for about 15 min. The brown suspension was then filtered hot (N₂), and the filtered solution was allowed to cool very slowly to room temperature. After 1–2 days, big crystals of I having a brown-black color were found on the walls of the container. I is practically insoluble in the hydrocarbon solvents at room temperature.

Anal. Calcd. for PdAl₂Cl₇C₆H₆: Pd, 21.91; Al, 11.08; Cl, 50.97; C, 14.85; H, 1.24. Found: Pd, 20.9; Al, 11.7; Cl, 51.4; C, 14.6; H, 1.13.

Complex I reacts at room temperature with tetrahydrofuran giving PdCl₂ and metallic Pd (in equivalent amounts), AlCl₃, and C₆H₆. Gas chromatographic determinations of benzene in the tetrahydrofuran solution gave values corresponding to the theoretical.

The crystal and molecular structure of I is being investigated by single crystal X-ray methods. After correction for absorption, the intensities of about 900 observable reflections, taken with the Cu K α radiation, have been visually estimated for the (*hk*0) and (*hk*1), (*hk*2), and (*h*01) and (*0*kl) reciprocal layers.

The triclinic unit cell of I has the following dimensions: *a* = 9.42 \pm 0.04, *b* = 9.24 \pm 0.04, *c* = 9.56 \pm 0.04 Å.; α = 77.9 \pm 0.7°, β = 96.2 \pm 0.7°, γ = 108.1 \pm 0.7°.

The experimental density of 2.07 g./cm.³ is in good agreement with the calculated value of 2.09 g./cm.³ based on one molecule per unit cell. The space group has been found to be P $\bar{1}$; the molecule is therefore centrosymmetrical.

The crystal structure has been roughly deduced by application of the usual heavy atom technique on three two-dimensional projections, in which all the higher atoms were introduced stepwise. The atomic coordinates and isotropic thermal factors have been refined by normal and modulated difference Fourier syntheses until the agreement factor over all the observed reflections has dropped to the value *R* = 0.152. A three-dimensional refinement of the structure is now in progress in our laboratory.

We will expose in the following the preliminary results of our X-ray analysis.

The molecular structure (Figure 1) consists of a central nucleus in which two palladium atoms are bonded together and two benzene rings are symmetrically disposed around the Pd–Pd axis, so as to give rise to a sandwich coordination around the two central atoms; the two (Al₂Cl₇) groups are symmetrically coordinated to the nucleus, via Cl–Pd bonds. The Pd–Pd distance of 2.58 \pm 0.01 Å. represents the shortest value so far found for this intermetallic bond.³

The Pd^I–C^I, Pd^I–C^{II}, Pd^{II}–C^{IV}, and Pd^{II}–C^V distances are 2.34 Å. on the average; no significant difference between them may be deduced from the actually available data.

The Pd^I–C^{III}, Pd^I–C^{VI}, Pd^{II}–C^{III}, and Pd^{II}–C^{VI} distances also are similar, with an average value of 2.94 Å. No significant deviation from the regular hexagonal symmetry has been assessed hitherto for the

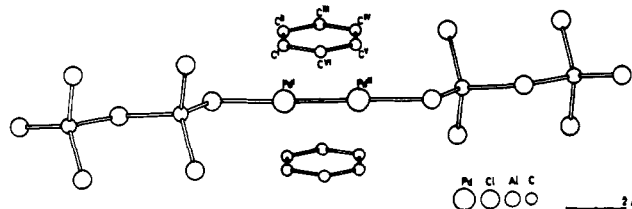


Figure 1. Side view of the [PdAl₂Cl₇(C₆H₆)₂]₂ molecule as it results from the present state of structural refinement. The black spot between the two palladium atoms represents the molecular and also crystallographic center of symmetry.

benzene rings (*d*_{C–C} \cong 1.41 Å.). The Pd–Cl distance has been found to be 2.46 \pm 0.02 Å., while the Cl–Pd–Pd–Cl group is approximately on a straight line (\angle Cl–Pd–Pd = 176 \pm 1°).

The resulting geometrical structure of the (Al₂Cl₇) ligands is in substantial agreement with the X-ray results quoted for other compounds of aluminum in tetrahedral coordination, containing bridge bonds.⁴ The bridge (Al–Cl) distances are longer (2.25 Å., av.) than the nonbridge distances (2.08 Å., av.); the \angle Cl–Al–Cl bond angles appear to deviate by \pm 10° with respect to the normal tetrahedral value (109.5°) so as to give rise to fairly close distances between chlorine atoms linked to the same aluminum atom.

As it has been pointed out previously, a completely new feature which results from the present picture is the binuclear sandwich coordination of the two Pd atoms by benzene rings.

It may be interesting to observe that, assuming the Pd–Pd and Cl–Pd to be purely single bonds, the xenon electronic configuration is attained if each benzene ring is formally assumed to contribute three π -electrons to each of the two palladium atoms; this qualitative picture is in agreement with the observed diamagnetism of the substance.

(4) P. H. Lewis, and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953); G. Allegra, G. Perego, and A. Immirzi, *Makromol. Chem.*, **61**, 69 (1963).

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The Crystal Structure of Monoclinic (β) Sulfur

Sir:

Above 95.39° the stable crystalline form of elemental sulfur is the monoclinic (β) phase. The unit cell dimensions obtained at 103° by Burwell¹ are *a* = 11.02, *b* = 10.96, *c* = 10.90 Å., β = 96.7°. The space group suggested by systematic extinctions is P2₁/c. The observed density of 1.96 g./cc. indicates that there are 48 atoms per unit cell. The predominant molecular species below the melting point is the S₈ ring, which in orthorhombic sulfur has the crown configuration of ideal symmetry D_{4d}– $\bar{8}2m$.² Six S₈ molecules can be accommodated in a unit cell of space group P2₁/c by placing four in general positions and two in special positions or by using three sets of special positions. The

(2) E. O. Fischer, and W. Hafner, *Z. Naturforsch.*, **10b**, 655 (1955).

(3) R. S. Nyholm, Proceedings of the 8th International Conference on Coordination Chemistry, Vienna, Sept. 1964.

(1) J. T. Burwell, *Z. Krist.*, **97**, 123 (1937).

(2) B. E. Warren and J. T. Burwell, *J. Chem. Phys.*, **3**, 6 (1935).

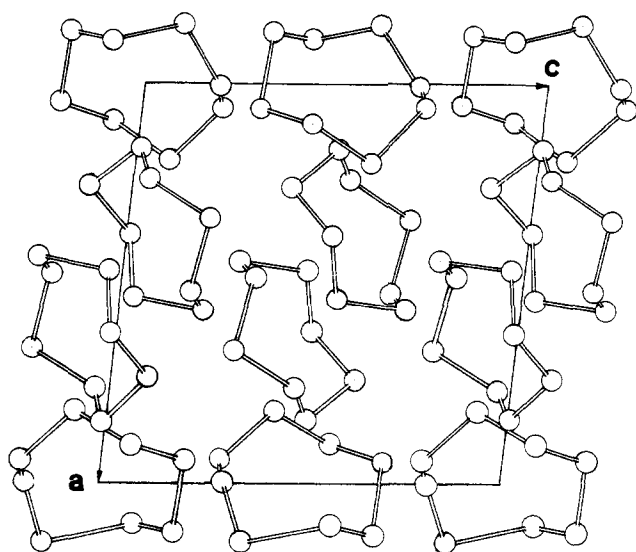


Figure 1. The structure of monoclinic sulfur. Each twofold molecule may have either the orientation shown at $x = 0$ or the orientation shown at $x = 1$.

special positions require centrosymmetric molecules, but the crown configuration is not centrosymmetric. A reasonable explanation is that the molecules which occupy special positions are disordered.

The structure of monoclinic sulfur has been determined from single crystal data. Crystals prepared from purified sulfur and annealed at 100° may be maintained at room temperature for up to a month. Complete data were collected by visually estimating the intensities on Weissenberg and precession photographs of these crystals. Enough signs to produce a recognizable Fourier were obtained by solving the Sayre-Cochran-Zachariasen relationship with the aid of Beurskens' IBM 1620 program.³ The details of the determination and of the refinements will be published later. The discrepancy index $R = \Sigma|F_o - F_c|/\Sigma|F_o|$ is presently 0.131 for 1270 observed reflections.

Table I. Atomic Parameters in Monoclinic Sulfur

Atom	x	y	z	Atom	x	y	z
1	0.234	0.525	0.031	9	0.182	-0.108	0.081
2	0.152	0.356	0.006	10	0.052	-0.069	0.206
3	0.256	0.252	-0.101	11	0.004	0.113	0.188
4	0.374	0.144	0.014	12	-0.152	0.126	0.079
5	0.537	0.228	0.037	13	-0.119	0.171	-0.093
6	0.553	0.315	0.208	14	-0.129	0.009	-0.193
7	0.512	0.498	0.176	15	0.053	-0.048	-0.201
8	0.332	0.525	0.202	16	0.094	-0.185	-0.073

The unit cell (Figure 1) contains four S_8 crowns in general positions 4(e) of space group $P2_1/c$: $\pm(x, y, z; x, 1/2 - y, 1/2 + z)$ with $x = 0.367$, $y = 0.356$, and $z = 0.072$. The remaining two molecules occupy the special positions 2(a): $0, 0, 0; 0, 1/2, 1/2$. Each molecule in 2(a) can assume one of two possible orientations, related by a center of inversion; these are indicated in Figure 1 by different orientations at $x = 0$ and at $x = 1$. The atomic coordinates are listed in Table I.

(3) P. T. Beurskens, *Acta Cryst.*, **17**, 462 (1964); P. T. Beurskens, "Technical Report on Sign Correlation by the Sayre Equation," Crystallography Laboratory, University of Pittsburgh, 1963.

The random orientations of the molecules in 2(a) are taken into account in the calculations by giving atoms 9 through 16 weights of one-half.

At the present stage of refinement the average bond length for each crystallographic type of molecule is 2.06 \AA . The average isotropic temperature factors are 3.6 \AA^2 for the molecules in 4(e) and 5.1 \AA^2 for the molecules in 2(a). The intermolecular contacts (minimum 3.38 \AA) are comparable to those in orthorhombic sulfur and in rhombohedral sulfur.⁴

This disordered arrangement leads to a residual entropy of $R/3 \ln 2$ per mole of S_8 molecules, or $0.057 \text{ e.u./g.-atom}$ of sulfur. The experimental entropy, based on the available heat capacity and enthalpy data for orthorhombic and monoclinic sulfur,⁵ is $0.045 \pm 0.050 \text{ e.u./g.-atom}$.

(4) J. Donohue, A. Caron, and E. Goldish, *J. Am. Chem. Soc.*, **83**, 3748 (1961).

(5) E. D. Eastman and W. C. McGavock, *ibid.*, **59**, 145 (1937); E. D. West, *ibid.*, **81**, 29 (1959).

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The Influence of Ionic Strength on Polarographic Half-Wave Potentials. IV. Theoretical Considerations Involving Systems of Mixed Uni-Univalent Inert Electrolytes

Sir:

In an earlier communication,¹ we have shown that the shift in the half-wave potential of cadmium, in systems of mixed uni-univalent nitrate inert (supporting) electrolytes, followed the empirical relationship.

$$(E_{1/2})_{\text{obsd}} = (E_{1/2})_{\mu=0} + (\Delta E_{1/2})_{\text{obsd}} = (E_{1/2})_{\mu=0} + N_a(\Delta E_{1/2})_a + N_b(\Delta E_{1/2})_b \quad (1)$$

where $(E_{1/2})_{\mu=0}$ is the half-wave potential of cadmium at zero inert electrolyte concentration, and N_a and N_b are the mole fractions of inert electrolytes a and b, respectively. The half-wave potential shifts, $(\Delta E_{1/2})_a$ and $(\Delta E_{1/2})_b$, are the predicted shifts in systems of electrolyte a or b alone and have been theoretically shown to be² (in mv.)

$$(\Delta E_{1/2})_{a \text{ or } b} \cong \{29.5 \log \gamma_{\pm} + 4.62m\phi\}_{a \text{ or } b} \quad (2)$$

where γ_{\pm} is the mean activity coefficient and ϕ is the osmotic coefficient of electrolyte a or b, respectively. It is the purpose of this investigation to show that eq. 1 possesses some theoretical significance.

If the effect of the electrolytes a and b on the change in the half-wave potential for cadmium is a purely extensive one, then eq. 2 for systems of mixed electrolytes would become

$$(\Delta E_{1/2})_{\text{obsd}} = \{29.5 \log (\gamma_{\pm})_t + 4.62m\phi_t\} \quad (3)$$

where m is the total molality and $(\gamma_{\pm})_t$ and ϕ_t are the total activity and osmotic coefficients of the system, respectively.

When the two inert electrolytes have an ion in com-

(1) Part II: N. E. Vanderborgh and D. E. Sellers, *J. Am. Chem. Soc.*, **86**, 2790 (1964).

(2) D. E. Sellers and N. E. Vanderborgh, *ibid.*, **86**, 1934 (1964).