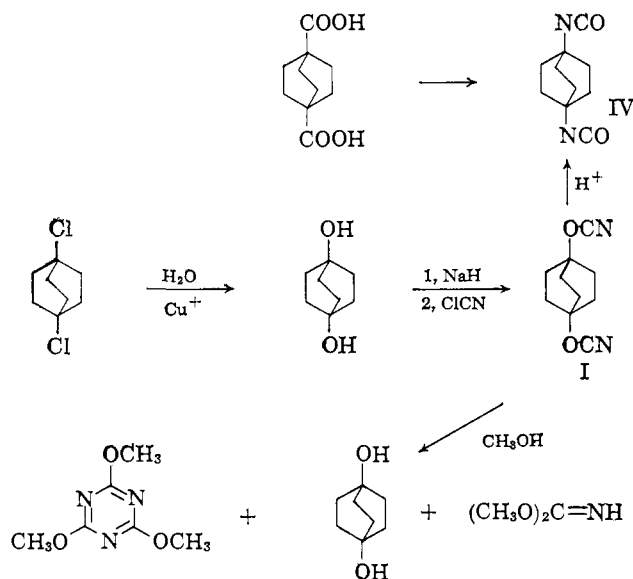


These compounds exhibited intense C–O–C absorptions at *ca.* 1120 cm^{-1} and strong $\text{C}\equiv\text{N}$ absorptions (doublets, probably because of Fermi resonance splittings) at 2220–2280 cm^{-1} of about one-fourth the intensity of that of the corresponding isocyanate.

cis-3-Ethoxy-2,2,4,4-tetramethylcyclobutan-1-ol (m.p. 56–57°) was prepared by successive reaction of *cis*-tetramethylcyclobutanediol with 1 mole of sodium hydride and excess ethyl bromide. 1,4-Dihydroxybicyclo[2.2.2]octane (m.p. 281–282°) was prepared by hydrolysis of 1,4-dichlorobicyclo[2.2.2]octane³ at 215° in the presence of cuprous ion.

The dicyanate (I) rearranged to the diisocyanate (IV, m.p. 111.5–112) when treated with boron trifluoride etherate or when eluted with benzene through a column of acid-washed alumina. The product was identical (mixture melting point, infrared spectrum) with a sample prepared⁴ by the Curtius reaction of bicyclo[2.2.2]octane-1,4-dicarboxylic acid.⁵ This rearrangement is strongly reminiscent of the corresponding rearrangement of thiocyanates to isothiocyanates which has been shown to proceed by an ionization-recombination process.⁶

Compound I reacted with methanol to yield 1,4-dihydroxybicyclo[2.2.2]octane, dimethyl iminocarbonate, and trimethyl cyanurate. These interconversions verify the structural assignments.



Preliminary results suggest that cyanates may have synthetic utility for the conversion of hydroxyl substituents to nitrogen functions using the sequence $\text{ROH} \rightarrow \text{ROCN} \rightarrow \text{RNCO}$. Details and further examples will appear in a subsequent paper.

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1,5-Cyclooctadiene Complexes of Gold(I) and Gold(III)

Sir:

Recent reviews^{1,2} note the fact that olefin complexes of gold have not been isolated, although an auric-styrene complex has been postulated as an unstable intermediate in the reduction of some gold complexes by styrene.³ Both Au(III) and Au(I) olefin complexes might well be expected to exist, being isoelectronic with Pt(II) and Ag(I), respectively, which form well-defined olefin complexes.

The isolation of two gold complexes with 1,5-cyclooctadiene is now reported. Mixtures of chloroauric acid and olefins in ether were found to be decolorized by ultraviolet light prior to their reduction to gold metal. In the case of 1,5-cyclooctadiene, white crystals (I) were formed which were washed with ether and dried *in vacuo*. Compound I is insoluble in common organic solvents such as chloroform, acetone, and alcohols and slowly decomposes, particularly in the presence of light. *Anal.* Calcd. for $\text{Au}_2\text{Cl}_2\text{C}_8\text{H}_{12}$: Au, 68.7; C, 16.8; H, 2.1; Cl, 12.4. Found: Au, 67.3; C, 17.4; H, 2.4; Cl, 12.6. An infrared spectrum of I in KBr showed the following absorptions: 3000 (w), 2975 (w), 2950 (w), 2930 (m), 2880 (m), 2820 (m), 1490 (m), 1430 (m), 1340 (m), 1240 (m), 1130 (s), 1073 (s), 1000 (m), 990 (m), 885 (s), 865 (m), 800 (s), 725 (s), 650 (m), 610 (s), 575 (s), and 450 (s) cm^{-1} . The same complex was formed from solutions containing isopropyl alcohol. Aurous chloride also forms I by warming with 1,5-cyclooctadiene and ethanol. At room temperature, however, and in the absence of ethanol and light, a small amount of another light-sensitive white solid was found (II), having a completely different infrared spectrum: 3000 (w), 2980 (m), 2940 (m), 2890 (w), 2880 (w), 1530 (m), 1520 (s), 1455 (s), 1410 (s), 1385 (m), 1245 (s), 1195 (m), 1045 (s), 1015 (s), 1000 (m), 930 (m), 895 (m), 815 (m), 775 (s), 590 (s), 530 (m), and 440 (m) cm^{-1} .

Chloroauric acid, when warmed with 1,5-cyclooctadiene in solutions of ethers or glycol ethers, gave white solids identified as mixtures of I and II from their infrared spectra. *Anal.* (for one such mixture). Calcd. for $\text{AuCl}_3\text{C}_8\text{H}_{12}$: Au, 48.0; C, 23.4; H, 2.9; Cl, 25.9. Found: Au, 53.3; C, 22.3; H, 3.0; Cl, 21.7. A mixture of 22.4% ($\text{AuCl}_3\text{C}_8\text{H}_{12}$) and 77.6% $\text{AuCl}_3\text{C}_8\text{H}_{12}$ would require: Au, 51.7; C, 22.0; H, 2.7; Cl, 22.9. II therefore appears to be $\text{AuCl}_3 \cdot \text{C}_8\text{H}_{12}$. Its formation from aurous chloride is not too surprising in view of the ready disproportionation of aurous to auric and gold metal. Presumably in the presence of ethanol, a reduction of II to I also occurs. II was found to have a slight solubility in carbon tetrachloride and a higher solubility in chloroform, though insufficient for identification by n.m.r. Both I and II gave 1,5-cyclooctadiene as the only volatile material on warming to 50° with triphenylphosphine in carbon tetrachloride. Heating I and II alone also gave 1,5-cyclooctadiene, the decomposition proceeding rapidly at 170 and 140°, respectively.

Two possibilities must be considered for the structure of each of these complexes: (1) a simple olefin

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complex, and (2) an allyl complex in which one of the chlorines or an additional hydrogen has added to the ring. The latter possibility merits serious consideration in view of the recent finding that butadiene-palladium chloride appears to be an allyl complex.⁴ However, the chlorine attached to carbon in these allyl complexes has been found to be labile and readily displaced by alkoxy. No such alkoxy compound has been found in the case of the gold complexes. When an ethanolic solution of chloroauric acid is warmed with 1,5-cyclooctadiene in the presence of sodium carbonate, I is formed in place of II.

Compound I is therefore tentatively identified as an aurous and II as an auric complex of 1,5-cyclooctadiene. The formulation of I as an olefin complex is consistent with the identification of the infrared absorption at 1530 and 1520 cm^{-1} as being due to a carbon double bond stretching frequency. Infrared absorptions in I and II at 3000 cm^{-1} are identified as being due to olefinic CH stretching frequencies.

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RECEIVED SEPTEMBER 21, 1964

Effect of Inert Gas Pressure and Solubility on Electrical Conductance in Fused Salts

Sir:

We wish to present a preliminary report on recent data resulting from a study of the mechanism of electrical conductance in pure fused salts.

A 500-ml. capacity Inconel metal bomb, Type A24-3HC5 of the Parr Instrument Co., was fitted with two CONAX thermocouple glands packed with a natural magnesium silicate. One of these glands contains a Chromel-Alumel thermocouple, and the other contains a pair of 20-gauge platinum wires for conductance electrodes. Pyrex bomb liners were prepared with capillary conductance cells fixed rigidly within them. In a typical experiment, such a liner-cell is charged with about 450 g. of dry NaNO_3 weighed to the nearest 0.5 g. Argon is admitted at room temperature into the sealed, evacuated bomb, containing the liner-cell and its salt charge, to a desired pressure. The number of moles of Ar introduced is calculated with the aid of the compressibility factor chart of Maslan and Littman¹ using the equilibrium values of pressure, room temperature, and the gas volume (known from the total volume of the bomb less the volumes of the liner-cell and its salt charge). The bomb is then heated in a furnace to a new temperature well above the melting point of NaNO_3 . Conductance measurements are made on the fused salt at equilibrium temperature and pressure. The number of moles of gaseous Ar still remaining is calculated from the new values of equilibrium temperature, pressure, and gas volume (the old volume corrected for change in density of the salt and its compression) with the aid of the same compressibility chart. Decrease in moles of gaseous Ar is attributed to its solubility in the melt, the latter then being calculated. The gas is slowly evacuated from the system, and the latter is pumped out to remove all Ar from the melt. New conductance

readings are then taken on the gas-free melt at the same temperature.

First results for NaNO_3 , using a capillary conductance cell of about 184-cm^{-1} cell constant, indicate a 5.7% decrease in specific conductance when the melt at 369° was subjected to 362 atm. of Ar. The conductance measurements showed excellent precision for both the gas-saturated and gas-free melt, yielding specific conductances of $1.16\text{ ohm}^{-1}\text{ cm}^{-1}$ for the melt under pressure, and $1.23\text{ ohm}^{-1}\text{ cm}^{-1}$ for the normal liquid, both at 369° . Maximum experimental error in these values is believed to be less than $\pm 0.01\text{ ohm}^{-1}\text{ cm}^{-1}$. The Henry's law constant determined for the solubility of Ar in fused NaNO_3 under these conditions, based on two independent determinations, was 18.7×10^{-7} and 19.6×10^{-7} mole of Ar (cm^3 of melt) $^{-1}$ atm. $^{-1}$.

We believe that the observed conductance decrease under pressure is due to loss of free volume available for transport in the melt. In the hole theory of fused salts, the volume increase on melting, ΔV , is attributed almost entirely to holes.² For NaNO_3 this is 4.32 cm^3 mole $^{-1}$, or a 10.7% volume increase.³ The isothermal compressibility coefficient, β_T , for fused NaNO_3 is about $20.4 \times 10^{-12}\text{ cm}^2$ dyne $^{-1}$ at 370° , based on interpolation of the data of Bockris and Richards.⁴ Using these data in conjunction with a density of 1.87 g. cm^{-3} for NaNO_3 at 369° ,⁵ we arrive at an approximate upper limit loss of holes of about 8.8% due to compression by 362 atm. of Ar alone. Thus, if hole density is the major factor controlling conductance of a pure fused salt,⁶ we would expect an approximate upper limit conductance decrease of fused NaNO_3 of 8.8% under these conditions owing to compression alone. This is not irreconcilable with our observed 5.7% decrease. On the other hand, the theoretical molar density of holes in a pure fused salt is given as⁴

$$N_{\text{H}} = (\Delta V/0.68)(\gamma/kT)^{3/4}$$

where γ is the liquid-vapor surface tension, k is Boltzmann's constant, and T is the absolute temperature. Using this equation with a value of $\gamma = 113.5$ dynes cm^{-1} at 369° ,⁷ in conjunction with the density of NaNO_3 , the volume density of holes is 4.86×10^{21} holes cm^{-3} . Our average Henry's law constant together with this figure reveals that if Ar atoms dissolve by occupying existing holes, about 8.6% of the holes would be occupied and thereby removed from the conductance mechanism. This value is also not at odds with the observed conductance decrease. Considered separately, the theoretical conductance decrease due to either compression of the melt or gas solubility alone is in line with observation. There can be no doubt that free volume is reduced by compression of the melt, but it may be doubtful if inert gas molecules dissolve by occupying existing holes. The positive enthalpies of solution observed by Grimes, Smith, and Watson⁸ may well indicate that solution occurs by the molecules

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