positions of the dolomite and calcite differ by the expected amount, and in the correct direction, does not prove that dolomite is a primary chemical precipitate, nor does it exclude this possibility as the data presented by Degens and Epstein do. The Flagstaff data do suggest, however, that isotopic equilibration between calcite and dolomite can occur at relatively low temperatures. Whether equilibration occurs when calcite and dolomite are coprecipitated, or later by penecontemporaneous dolomitization of unconsolidated sediments, remains an unanswered question.

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Mononuclear and Polynuclear Chemistry of Rhenium (III): Its Pronounced Homophilicity

Abstract. *Extensive chemical, spectrophotometric, and x-ray structural studies have shown that trivalent rhenium is strongly homophilic—that is, it tends to form bonds to other* Re^{III} *atoms—and it forms at least three different series of* $[ReX_4]_n^{n-}$ *complexes. The mononuclear, square complex,* $[ReBr_4]^-$*, adds two water molecules to give* trans-$[ReBr_4(H_2O)_2]^-$. *The binuclear complexes* $[Re_2Cl_8]^{2-}$ *and* $[Re_2Br_8]^{2-}$ *have strong Re-Re bonds, unsupported by halide bridges. The trinuclear species,* $[Re_3X_{12}]^{3-}$ *or* $Re_3X_9L_3$*, contain the triangular* Re_3X_9 *clusters. Use of* $ReCl_3$ *appears always to lead directly to products containing* Re_3Cl_9*; this unit exists in* $ReCl_3$ *itself and does not appear to be kinetically labile. The* $[Re_2X_8]^{2-}$ *ions are obtained by reduction of* ReO_4^- *in aqueous HCl or HBr. Salts of* $[ReBr_4(H_2O)_2]^-$ *can be obtained directly from solutions of* $ReBr_3$ *in HBr along with numerous other compounds, some containing trinuclear clusters.*

A tendency for an atom to form bonds to one or more others of the same chemical identity may be termed homophilicity (*1*). While it is a pronounced property of many nontransition elements, it is much less common among transition elements. It appears to be favored by lower formal oxidation numbers (becoming quite pronounced for oxidation number zero) and higher atomic numbers. Among compounds exemplifying homophilicity (*2*) are the newly discovered trinuclear cluster compounds of rhenium(III) (*3–5*). The chemistry of rhenium(III) has now been investigated more comprehensively, the initial purpose being determination of the generality of occurrence of trinuclear clusters. The actual result has been the discovery that rhenium(III) forms at least three series of complexes, mono-, bi-, and trinuclear.

The parent compound for all known trinuclear chloro complexes is $ReCl_3$, which itself contains trinuclear clusters (*6*). It crystallizes in the space group $R\bar{3}m$, with 18 formula units per hexagonal cell. The six trinuclear clusters lie on the $6c$ positions and have $3m$ (C_{3v}) symmetry. All of the internal dimensions of the Re_3Cl_9 unit in crystalline $ReCl_3$ are approximately the same as corresponding dimensions in $[Re_3Cl_{12}]^{3-}$, $[Re_3Cl_{11}]^{2-}$, and $Re_3Cl_9(PEt_2Ph)_3$, at a stage of refinement of the $ReCl_3$ structure where the conventional residual stands at 16 percent.

All compounds of Re^{III} that we have prepared from $ReCl_3$, as well as all nonaqueous solutions of $ReCl_3$ and solutions in aqueous HCl, exhibit only the absorption bands in the near infrared, visible, and near ultraviolet, which we consider (*5*) to be characteristic of the Re_3Cl_9 cluster. It thus appears that this cluster is very stable—kinetically, at least, and perhaps also thermodynamically—and that it therefore forms a basis for "one of the chemistries" of trivalent rhenium.

In the Re^{III}-Br system, the analogous Re_3Br_9 cluster also is of some importance. The red-black $Re_3Br_9(PEt_2Ph)_3$ is isomorphous with $Re_3Cl_9(PEt_2Ph)_3$, and these two compounds have quite similar electronic absorption spectra. The compound $ReBr_3$ has not yet been obtained in crystals suitable for complete structure determination, but powder x-ray data suggest that the structure may be quite similar to that of $ReCl_3$, and solutions in both aqueous HBr and nonaqueous solvents exhibit spectra showing the presence of Re_3Br_9 clusters, though not exclusively. The structure of the clusters is such that internal strains caused by repulsion of nonbonded halogen atoms could perhaps become severe enough in the bromine case to labilize or destabilize (or both) the trinuclear structure relative to simpler ones.

A "second chemistry" of trivalent rhenium has for its chief structural feature binuclear species which have very short and strong Re-Re bonds without any halogen bridges. The simplest members of this class are the various salts of $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$, with cations, such as K^+, NH_4^+, and quaternary ammonium, phosphonium, and arsonium ions. These may be prepared by reductions of solutions of ReO_4^- in aqueous HCl or HBr with hypophosphite ion. Yields are quite sensitive to reaction conditions, varying from essentially zero under many circumstances to around 20 percent under optimum conditions. The $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ ions can be interconverted simply by heating the former in aqueous HBr and the latter in aqueous HCl. These compounds are actually the same types as, in some cases identical with, a series reported by Russian workers (*7*), but in our view the compounds were incorrectly identified and formulated by them (*8*) as Re^{II} complexes.

The compound $K_2Re_2Cl_8 \cdot 2H_2O$ crystallizes in the space group $P\bar{1}$ and contains one formula weight per unit cell. The $[Re_2Cl_8]^{2-}$ anion, which is required by the space group to be centric, has approximately D_{4h} symmetry. Some of its principal dimensions are shown in Fig. 1. The Re-Re distance (2.24 Å) is to be compared with that (2.48$_5$ Å) in the Re_3Cl_9 cluster (*2, 4, 5*). The water molecules are coordinated to the K^+ ions and not to the rhenium atoms.

The fact that $[Re_2Cl_8]^{2-}$ has an

eclipsed, rather than a staggered, structure (that is, not the structure to be expected on considering only the effects of repulsions between chlorine atoms) is satisfactorily explained when the Re-Re multiple bonding is examined in detail. To a first approximation, each rhenium atom uses a set of s, p_x, p_y, $d_{x^2-y^2}$ hydrid orbitals to form its four Re-Cl bonds. The remaining valence shell orbitals of each rhenium may then be used for metal-to-metal bonding as follows. (i) On each rhenium $d_{z^2} - p_z$ hybrids overlap to form a very strong σ bond. (ii) The d_{xz}, d_{yz} pair on each rhenium can be used to form two fairly strong π bonds. Neither the σ nor the π bonds impose any restriction on rotation about the Re-Re axis. These three bonding orbitals will be filled by six of the eight Re d electrons. (iii) There remains now, on each rhenium atom, a d_{xy} orbital containing one electron. In the eclipsed configuration these overlap to a fair extent (about one third as much as one of the π overlaps) to give a δ bond, with the two electrons becoming paired. This bonding scheme is in accord with the measured diamagnetism of the $[Re_2Cl_8]^{2-}$ ion. If, however, the molecule were to have a staggered configuration, the δ bonding would be entirely lost (d_{xy}-d_{xy} overlap would be zero). We believe that an absorption band at about 36,000 cm^{-1} can be assigned to the $\delta \rightarrow \delta^*$ transition (which is $a_{1g} \rightarrow b_{2u}$ electric-dipole-allowed with z polarization), thus fixing the energy of the δ bond at about 60 kcal/mole. Since the Cl-Cl repulsion energy tending to favor the staggered configuration can be estimated to be only a few kilocalories per mole, the δ-bond energy is decisive and stabilizes the eclipsed configuration. This would appear to be the first quadruple bond to be discovered.

This same structure has recently been reported (*9*) for a compound alleged (*7*) to be $(C_5H_5NH)HReCl_4$ and thus to contain Re(II). We have prepared this, and several other compounds, by the hydrogen reduction method of the Russian workers (*7*) and find that all of them appear to be identical with the compounds we consider to be binuclear Re^{III} compounds, the one already mentioned being simply the pyridinium salt of $[Re_2Cl_8]^{2-}$. The very short Re–Re distance reported by Kuznetzov and Koz'min (*9*) initially led us to suspect that their structure determination was in error, especially when the pronounced tendency of this compound to give twin crystals (as reported by Kuznetzov and Koz'min and confirmed by us) and the "trial and error" method of refinement were taken into account. The manner of twinning, which was not described by the Russian workers, is a rather subtle one, the twins appearing to be single tetragonal crystals because of the fact that one of the cell dimensions (8.25 Å) is almost exactly half of another (16.31 Å). We have concluded, however, that the work of Kuznetzov and Koz'min is correct in all essentials, the only significant discrepancy being in Re–Re distance for which they give 2.22 Å, while we have found a value of 2.24 Å. Possibly when all data are treated by full-matrix least-squares refinement, this discrepancy may lessen. It is pertinent that the eclipsed rotomer is also crystallographically required in the pyridinium compound where the point symmetry of the $[Re_2Cl_8]^{2-}$ ion is D_{2h}.

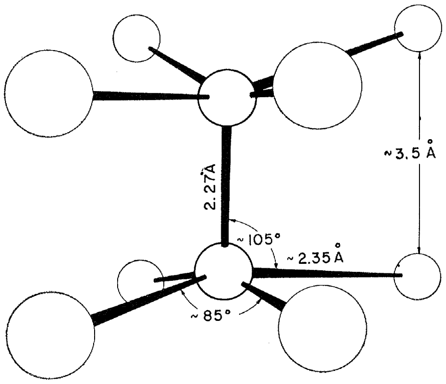

Fig. 1. The structure of the $[Re_2Cl_8]^{2-}$ ion found in $K_2Re_2Cl_8 \cdot 2H_2O$. Bond distances are in angstroms and angles in degrees. The symmetry is D_{4h} within the uncertainties of the dimensions. There is a rigorous (crystallographic) center of symmetry. The fully refined structure has Re–Re = 2.24Å.

Rhenium (III) is also capable of forming mononuclear complexes, which are either four- or six-coordinate. When $ReBr_3$ is dissolved in concentrated aqueous HBr, a quaternary ammonium bromide added, and the solution heated several hours, red [mononuclear Re (III)], yellow [Re(IV)], and black salts are precipitated in crystalline form. Ruby red $(C_2H_5)_4N[ReBr_4(H_2O)_2]$, prepared in this manner, has been subjected to single-crystal x-ray structure determination and found to contain *trans*-$[ReBr_4(H_2O)_2]^-$ ions. On heating in a vacuum, this compound loses weight corresponding to $2H_2O$, and the characteristic infrared bands of H_2O disappear, leaving yellow-brown $(C_2H_5)_4N[ReBr_4]$. The latter compound has a visible absorption spectrum quite different from that of the various $[Re_3Br_8]^{2-}$ compounds and from the spectrum which is characteristic of compounds containing Re_3Br_9 clusters. It does resemble that of the dihydrate, however, and, when the compound is dissolved in acetone, it gives a dark yellow solution with a visible spectrum very similar to that of *trans*-$[ReBr_4(H_2O)_2]^-$. The acetone solution presumably contains $[ReBr_4(C_2H_6CO)_2]^-$ ions. Further evidence of the existence of red, diamagnetic, square $[ReBr_4]^-$ was obtained with red-orange $CsReBr_4$. This has a visible spectrum essentially the same as that of the previously mentioned $(C_2H_5)_4NReBr_4$ and it is isomorphous with $CsAuBr_4$, a compound which may be assumed with some certainty to contain a square mononegative anion, $[AuBr_4]^-$.

Solutions of $ReBr_3$ in HBr also afford various other compounds which contain metal atom clusters. Crystallographic work, still in progress, has shown that a red-black compound, $(quinolinium)_2Re_4Br_{15}$, contains both Re_3 clusters and isolated Re atoms. When $(C_2H_5)_4N[ReBr_4(H_2O)_2]$ is heated in air, it is converted into a compound which we believe to contain the new oxybromo anion $[Re^{V}Br_2O_2]^-$. This structure is proposed, tentatively, on the basis of the weight loss in the conversion and the presence of two strong bands, at 938 (sharp) and at about 875 (broad) cm^{-1}, in the infrared spectrum. These bands are consistent with the presence of a nonlinear ReO_2 grouping. A great many more interesting compounds have been obtained from the Re^{III}-Br system and it is evident that the chemistry here is very extensive and very complicated.

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1. This word does not appear to have been used previously in any context, scientific or otherwise. It is derived, in an etymologically homogeneous way, from the Greek roots *hom-* (like or same) and *phil-* (loving). The opposite tendency, that of forming bonds to atoms of different chemical identity, might be called *heterophilicity*.

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8. We refer here specifically and only to the compounds formulated (*7*) as $M^{I}HReCl_4$, that is, as Re^{II} compounds. While direct, positive, and unequivocal proof that the indicated hydrogen atoms are not present, either as protons (*7*) or as hydride ions, is difficult, if not impossible, to obtain, there are a number of reasons for believing that they are absent. Actually, the only definite experimental data offered (*7*) to support the postulate that they are present as protons was the determination of valence state of the rhenium by alkaline chromate reduction. We have also made such measurements, and in our hands they lead to a valence state of 2.9 ± 0.4 for the rhenium.
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Hydrazine-Water System: The Water-Rich Eutectic

Abstract. *The melting point and composition of the water-rich eutectic of hydrazine and water have been determined by differential thermal analysis as 193° ± 0.5°K and 27 ± 1 mole percent hydrazine, respectively.*

The solid system, hydrazine-water, exhibits a monohydrate $N_2H_4 \cdot H_2O$ and two eutectic compositions. The monohydrate and the hydrazine-rich eutectic are easy to identify since crystallization in these composition ranges proceeds without difficulty. Their melting points have been reported as −51.7°C and −54°C, respectively, and the eutectic composition as 69 percent of hydrazine by weight (55.6 mole percent) (*1, 2*). Mohr and Audrieth (*1*) did not report values for the water-rich eutectic because of the strong tendency of these solutions to become supercooled. Mohr and Audrieth's diagram, however, clearly showed the existence of the water-rich eutectic. Hill and Sumner (*2*) determined a series of liquidus points as functions of composition and, by extrapolation, arrived at −90°C for the melting point and 40.5 percent (27.7 mole percent) of hydrazine by weight as the probable temperature and composition of the water-rich eutectic.

We have crystallized a eutectic containing 27 ± 1 mole percent of hydrazine melting at −80° ± 0.5°C. Differential thermal analysis of other water-rich samples has confirmed this value. Crystallizable low-temperature glasses are characterized by a fairly reproducible temperature of spontaneous crystallization during warm-up. Mixtures of otherwise crystallizable compounds may have ranges of composition within which crystallization does not occur. In these cases the interpolated values of the spontaneous crystallization temperature overlap and eventually exceed the interpolated values of the melting points. However, we found that crystallization appeared to be possible at all compositions with this system if it was properly conditioned. Conditions that would induce crystallization were then investigated. A well-known, though not well-understood, behavior of some of these systems is their capacity to crystallize after appropriate cooling, warming, and cooling again (*3*). Suspecting that our system might behave in this way, we applied this technique and succeeded in obtaining a well-crystallized eutectic containing 27 mole percent of hydrazine. Crystallization was always induced after a second cooling from a temperature between the spontaneous crystallization (extrapolated from other compositions) and the eutectic melting point temperatures, but it never occurred during the warming up period of samples cooled from temperatures above the eutectic's melting point. The apparatus used consisted of a copper-constantan thermocouple assembly permitting the recording of the temperature difference between the sample and a reference body as a function of the reference body temperature. The two samples were cooled and warmed up in a copper block that furnished a controlled homogeneous temperature. The samples were cooled by immersion in liquid nitrogen. The samples were warmed up at rates of the order of 3°K per minute between 77° and 200°K and lower near room temperature. The sample tubes were sealed test tubes with an inner, thin-walled capillary that housed the thermocouples and was filled with benzene to assure good thermal contact. The reference junction for measuring the reference body temperature was kept in liquid nitrogen. Benzene was used as the reference body since it does not exhibit any transformation at temperatures between that of liquid nitrogen and its melting point (5.51°C). The samples were prepared by weighing distilled water and hydrazine of reagent quality. The temperature difference was plotted against the reference temperature by means of an *X-Y* recorder having a sensitivity of 0.1 mv/in. (0.25 mv/cm) and 0.5 mv/in. (1.3 mv/cm) in the $Y(T_S\text{-}T_R)$ and $X(T_R)$ axes, respectively. Figure 1 shows the warm-up curve of a water-rich sample of 24.8 percent of hydrazine by weight (15.6 mole percent). The four stages represent (i) glass transformation, characterized by a change in specific heat; (ii) spontaneous crystallization, char-

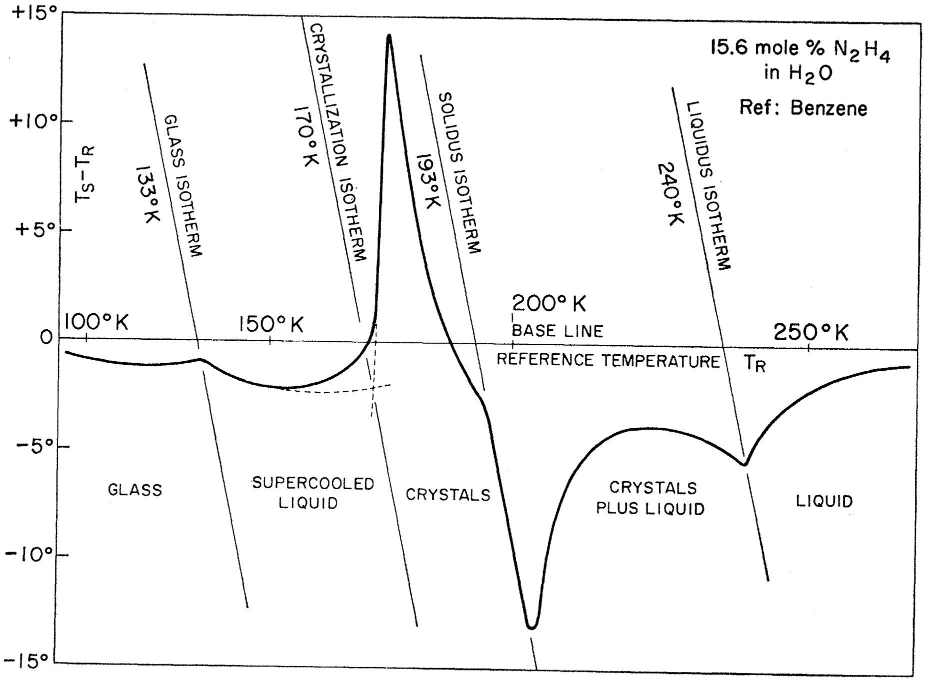

Fig. 1. Differential thermal analysis warm-up recording of a 15.6 mole percent of hydrazine solution in water showing (i) the glass transformation at 133°K, (ii) the spontaneous crystallization occurring at 170°K, (iii) the solidus point at 193°K, and (iv) the liquidus point at 240°K.