ligands containing phosphorus, and it thus appears probable that "mixed" ligands containing both phosphorus and sulfur would yield much the same results as have been reported above.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASSACHUSETTS 02139

Some Reactions of the Octahalodirhenate(III) Ions. V. Polarographic Reduction[1]

BY F. A. COTTON, W. R. ROBINSON, AND R. A. WALTON

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Relatively few studies of the redox reactions of metal atom cluster compounds have been published.[2,3] In those reported, the results (for M_6X_{12} species) have been remarkably consistent with the molecular orbital description of the bonding given by Cotton and Haas[4] for such systems. A comparable sort of MO analysis of the bonding[5,6] has been carried out for the $Re_2X_8^{2-}$ species (X = Cl, Br, and most recently,[7] NCS) which have D_{4h} symmetry. This treatment, which should also be applicable in its general features to any analogous technetium complexes, leads to the conclusion that there are two relatively low-lying, nonbonding σ orbitals which are directed outward along the fourfold axis of the molecule.

It would seem reasonable to suppose that at least one and perhaps two electrons could be added to these orbitals, thus forming $Re_2X_8^{3-}$ and $Re_2X_8^{4-}$ species, without interfering with any of the components, σ, π, or δ, of the Re–Re bond. Hence, the extremely short metal–metal distance and the eclipsed configuration should be maintained in the reduced species. Whether the $Re_2X_8^{4-}$ species should have zero or two unpaired electrons will depend on how nearly degenerate the two nonbonding σ orbitals are; this is difficult to predict with confidence.

The investigations described here were undertaken to test the foregoing ideas. The results are also relevant to the question of why the only known $Tc_2X_8^{n-}$ species[8,9] is $Tc_2Cl_8^{3-}$.

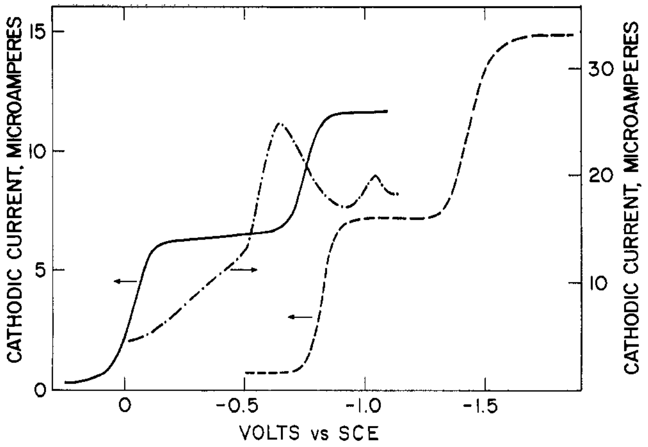

Figure 1.—Polarograms for the tetra-*n*-butylammonium salts of $Re_2Cl_8^{2-}$ (------), $Re_2(NCS)_8^{2-}$ (——), and $Re_2Br_8^{2-}$(–·–·–) in acetonitrile at 25°.

Experimental Section

The compounds $[(n\text{-}C_4H_9)_4N]_2[Re_2X_8]$, X = Cl, Br, NCS, were prepared as described elsewhere.[7,10] Approximately 10^{-3} *M* solutions in acetonitrile containing 0.5 *M* tetra-*n*-butylammonium perchlorate as supporting electrolyte were used to record the polarograms. The results are displayed in Figure 1 and numerical results pertaining to the $Re_2Cl_8^{2-}$ and $Re_2(NCS)_8^{2-}$ ions are summarized in Table I.

TABLE I

POLAROGRAPHIC DATA FOR $Re_2Cl_8^{2-}$ AND $Re_2(NCS)_8^{2-}$ IN ACETONITRILE[a] AT 25°

Step	$E_{1/2}$[b]	n	i_d[c]	I_d[d]	$E_{3/4} - E_{1/4}$, mv
		1.083 m*M* $[(C_4H_9)_4N]_2Re_2Cl_8$			
1	−0.82	1.1	6.54	2.80	65 ± 3
2	−1.44	~1.3	7.42	...	93 ± 3
		0.800 m*M* $[(C_4H_9)_4N]_2Re_2(NCS)_8$			
1	−0.04	1.1	5.5	2.7	65 ± 3
2	−0.71	1.1	4.6	2.6	59 ± 4

[a] 0.5 *M* $[(n\text{-}C_4H_9)_4N]ClO_4$ added as supporting electrolyte. [b] With respect to the standard calomel electrode, in volts. [c] Average limiting current in microamps. [d] $I_d = i_d/CM^{2/3}t^{1/6}$, where *C* = concentration, *M* = mercury flow rate, and *t* = time between drops.

Discussion

Both the $Re_2Cl_8^{2-}$ and the $Re_2(NCS)_8^{2-}$ salts gave conventional two-wave reduction polarograms. There are no simple reduction waves in the polarogram of $Re_2Br_8^{2-}$ although reduction obviously occurs. This polarogram will not be discussed further.

The number, *n*, of electrons involved in the reductions of the $Re_2Cl_8^{2-}$ and $Re_2(NCS)_8^{2-}$ ions was estimated using the Ilkovic equation,[11] and these are recorded in Table I. The required values of *D*, the diffusion coef-

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ficient, were calculated from the expression[12] $D = RT\lambda_0/zF$, in which R is the gas constant, T is the Kelvin temperature, z is the charge on the ion before reduction, F is the Faraday, and λ_0 is the equivalent conductance (in acetonitrile) at infinite dilution of the ion being reduced. Values of 63 and 59 were used for λ_0 for $Re_2Cl_8^{2-}$ and $Re_2(NCS)_8^{2-}$, respectively.[13] It can be seen that the calculated values, with the possible exception of that for step 2 in the reduction of $Re_2Cl_8^{2-}$, are satisfactorily close to 1.0.

The appearance of the polarographic waves suggests that the reductions are reversible. To test this more rigorously, the $E_{3/4} - E_{1/4}$ values were measured. For reversibility, these should be about 60 mv.[14] For all but step 2 in the $Re_2Cl_8^{2-}$ reduction the agreement is good. It thus appears that while the $Re_2Cl_8^{3-} + e \rightarrow Re_2Cl_8^{4-}$ reduction may not be a simple, reversible process, the others are reversible redox processes represented by the general equation

$$Re_2X_8^{n-} + e = Re_2X_8^{(n+1)-}$$

Conclusions

The results obtained are in agreement with the qualitative predictions made from the bonding scheme, insofar as one-electron reductions of $Re_2X_8^{2-}$ species to give $Re_2X_8^{3-}$ and $Re_2X_8^{4-}$ species evidently occur. It remains to be seen whether these reduced species will have the expected structural characteristics and whether the $Re_2X_8^{4-}$ species will have two unpaired electrons or none. These results may not be easy to obtain because the very negative potentials required to produce the reduced species imply that isolation of salts may be very challenging. Moreover, because of the large quadrupole moments of the rhenium, chlorine, and nitrogen atoms in the reduced $Re_2X_8^{3-,4-}$ species, the detection of esr signals might also be expected to be difficult. Preliminary efforts have failed.

It is, however, possible to obtain some further support for the view that the reductions involve adding electrons to the nonbonding σ orbitals and therefore cause no important change in bonding or structure by referring to the $Tc_2Cl_8^{3-}$ ion. Although at the time this was first prepared[8] and structurally characterized[9] its charge of -3 in contrast to that of -2 for $Re_2Cl_8^{2-}$ was puzzling, it now seems clear that it is simply the analog of $Re_2Cl_8^{3-}$ whose existence we have demonstrated in the present study. Probably the $Tc_2Cl_8^{3-}$ ion is relatively more stable, in keeping with the general tendency for lower oxidation states to be more stable with the lighter transition metals in a given group.

Conversely, the fact that $Tc_2Cl_8^{3-}$ possesses an eclipsed structure with a very short metal–metal bond is in agreement with our views as to the nature of the reduction process.

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[12] *Cf.* G. W. C. Milner, "The Principles and Applications of Polarography," Longmans, Green and Co., New York, N. Y., 1957, p 40.

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Contribution from the Department of Chemistry,
Oregon State University, Corvallis, Oregon 97331

Neutral and Anionic Complexes of Copper(I) Chloride with Ethylamine[1a]

By James R. Clifton[1b] and John T. Yoke III

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Descriptions have been given of complex formation in the copper(I) chloride–triethylamine–triethylammonium chloride system[2] and the copper(I) chloride–diethylamine–diethylammonium chloride system.[3] A study of the copper(I) chloride–ethylamine–ethylammonium chloride system is now reported. These results are important in elucidating the products of the oxidation–reduction reactions between the amines and copper(II) chloride.[4]

Elsey[5] noted the interaction of copper(I) chloride and ethylamine, but did not establish the product. Peters[6] reported a series of complexes of methylamine with the copper(I) halides, and Wilkins and Burkin[7] prepared a number of such complexes with long-chain primary amines. Methylammonium chlorocuprate(I) complexes have been described by Remy and Laves.[8]

Experimental Section

Materials and Procedure.—These have been described previously.[2,3,9] The compounds prepared in this work were sensitive to moisture and rapidly discolored by traces of oxygen. The materials were handled in a high vacuum apparatus or under an inert atmosphere in a drybox.

The System Ethylamine–Copper(I) Chloride.—Copper(I) chloride was not appreciably soluble in an 11.4 molar excess of ethylamine at its boiling point. The 0° pressure–composition phase diagram of the system is shown in Figure 1. Ethylamine was removed by distillation in the vacuum system until constant weight was achieved, to give the white 1:1 complex, mp (sealed tube) 69°. *Anal.* Calcd for $CuCl \cdot C_2H_5NH_2$: mole ratio, 1.00; Cu, 44.1; Cl, 24.6; $C_2H_5NH_2$, 31.3. Found: mole ratio, 1.00; Cu, 43.7; Cl, 24.3; $C_2H_5NH_2$, 31.3. The complex was not soluble in carbon tetrachloride, dimethylformamide, tetrahydrofuran, or glyme and was very slightly soluble in dimethyl sulfoxide or nitrobenzene. The 2:1 complex, $CuCl \cdot 2C_2H_5NH_2$, was isolated by removing the excess of ethylamine (after a long period of equilibration with copper(I) chloride) until the point corresponding to mole ratio 2.00 in Figure 1 was attained. It was similarly insoluble in various solvents. The 3:1 complex had too high a dissociation pressure to permit handling it in the drybox.

Reaction of Ethylammonium Chloride with Copper(I) Chloride.—Ethylammonium chloride was prepared by saturating a solution of ethylamine in benzene with anhydrous hydrogen chloride. The mixture was boiled for 30 min and gave white crystals on cooling to room temperature. The product was very deliquescent. It was dried *in vacuo* over phosphorus pentoxide at 100° for 1 day and then pumped on in the high vacuum system at 100° for 6 hr; mp (sealed tube) 109°, lit. 109–110°. Twenty-millimole quantities of ethylammonium chloride and of copper(I) chloride

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[1] (a) Abstracted from the Ph.D. Dissertation of J. R. C., Oregon State University, 1967; (b) Weyerhaeuser Fellow, 1966–1967.

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