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.

---

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

[13] These values were calculated using the Λ_0 values from the previously reported[7] conductance measurements and taking $\lambda_0 = 62$ for $[(n\text{-}C_4H_9)_4N]^+$. See A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967).

[14] P. Zuman, *Progr. Polarog.*, **2**, 583 (1962).

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

Received January 30, 1967

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

---

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

[2] J. T. Yoke, J. F. Weiss, and G. Tollin, *Inorg. Chem.*, **2**, 1210 (1963).

[3] J. R. Clifton and J. T. Yoke, *ibid.*, **5**, 1630 (1966).

[4] J. R. Clifton and J. T. Yoke, to be published.

[5] H. M. Elsey, *J. Am. Chem. Soc.*, **42**, 2080, 2454 (1920).

[6] W. Peters, *Z. Anorg. Allgem. Chem.*, **89**, 191 (1914).

[7] R. G. Wilkins and A. R. Burkin, *J. Chem. Soc.*, 127 (1950).

[8] H. Remy and G. Laves, *Ber.*, **66**, 571 (1933).

[9] W. E. Hatfield and J. T. Yoke, *Inorg. Chem.*, **1**, 463 (1962).

were mixed in a reaction tube in the drybox. The tube was then attached to the vacuum system, and 15 ml of deoxygenated absolute alcohol and 4 mmoles of anhydrous hydrogen chloride were added. The solids dissolved when the tube was warmed to 40°. The tube was cooled in an ice bath, and white needles were deposited. These were removed by filtration, washed with absolute ethanol, then petroleum ether, and dried *in vacuo*, to give ethylammonium dichlorocuprate(I). *Anal.* Calcd for $C_2H_5NH_3CuCl_2$: Cu, 35.2; Cl, 39.3. Found: Cu, 35.0; Cl, 39.2.

The System Ethylamine–Ethylammonium Dichlorocuprate(I).—The 0° pressure–composition phase diagram of this system is shown in Figure 1. Ethylammonium dichlorocuprate(I) was very soluble in an excess of ethylamine at 0°. A solid phase was present only when the mole ratio of ethylamine to ethylammonium dichlorocuprate(I) was lower than 1.44. The equilibrium pressure dropped sharply to a negligible value at mole ratio 1.0, to give a white solid reaction product.

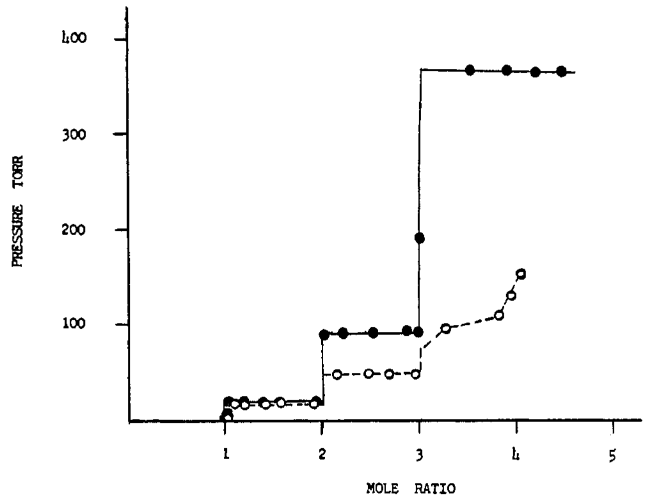


Figure 1.—0.0° isotherms: ●, $C_2H_5NH_2$–CuCl system; ○, $C_2H_5NH_2$–$C_2H_5NH_3CuCl_2$ system.

The System Ethylamine–Ethylammonium Chloride.—Ethylammonium chloride has been reported to be soluble in ethylamine at −33.5°.[5] The 0° pressure–composition phase diagram obtained in the present work indicated no compound formation in this system; the solubility at 0° was found to be approximately 0.9 mole of solute per mole of amine.

Results and Discussion

For the process $CuCl\cdot 3C_2H_5NH_2 \rightarrow CuCl\cdot 2C_2H_5NH_2 + C_2H_5NH_2$, the dissociation pressures were 18.0 torr at −22.9°, 88.5 torr at 0.0°, and 432 torr at 26.8°. By application of the Clausius–Clapeyron relation, the following thermodynamic functions at 0.0° were calculated for this process: $\Delta H^\circ = 2.49$ kcal/mole; $\Delta F^\circ = 0.773$ kcal/mole; $\Delta S^\circ = 6.3$ eu. In this calculation, ΔH_{vap} of ethylamine was taken as 7.06 kcal/mole on the basis of its vapor pressure–temperature relation, determined using both new and previously cited[9] experimental data. Because of its instability, the 3:1 complex was not further studied. Similar dissociation pressure studies for the process $CuCl\cdot 2C_2H_5NH_2 \rightarrow CuCl\cdot C_2H_5NH_2 + C_2H_5NH_2$ gave the values 15.0 torr at 0.0°, 125 torr at 25.5°, and 248 torr at 34.0°. For this process, the thermodynamic functions at 0.0° were: $\Delta H^\circ = 6.65$ kcal/mole; $\Delta F^\circ = 1.74$ kcal/mole; $\Delta S^\circ = 18.0$ eu. The 1:1 complex had a negligible dissociation pressure at room temperature.

The symmetric N–H stretching frequency was lowered from 3289 cm^{-1} in the free amine to 3150 cm^{-1} in the 2:1 complex and to 3120 cm^{-1} in the 1:1 complex. The asymmetric stretch was lowered from 3367 cm^{-1} in the free amine to 3200 cm^{-1} in the 1:1 complex; a doublet, at 3260 and 3240 cm^{-1}, was apparent in the spectrum of the 2:1 complex. The spectra indicated the absence of aminolysis.

No suitable solvent for molecular weight determinations was found. Wilkins and Burkin,[7] working with primary amines whose long chain lengths conferred enhanced solubility in hydrocarbon solvents, found $CuCl\cdot 2RNH_2$ complexes to be dimeric and $CuCl\cdot RNH_2$ complexes to be tetrameric. The ethylamine complexes are presumed to be similar. The third amine molecule, in the $CuCl\cdot 3C_2H_5NH_2$ complex, is held very loosely in the lattice and presumably is not specifically coordinated.

Ethylammonium dichlorocuprate(I) binds one, two, or three moles of ethylamine at 0°. The material of composition $C_2H_5NH_3CuCl_2\cdot 3C_2H_5NH_2$, a colorless liquid, may be formulated as the five-coordinate anionic complex. Its alternative formulation, as an equimolar mixture of ethylammonium chloride and $CuCl\cdot 3C_2H_5NH_2$, can be ruled out since the 3:1 neutral complex is an insoluble solid. Similarly, $C_2H_5NH_3CuCl_2\cdot 2C_2H_5NH_2$ is a liquid at 0° and can be formulated as a four-coordinate anionic complex. It cannot be a mixture of ethylammonium chloride and $CuCl\cdot 2C_2H_5NH_2$ since the latter is an insoluble solid; however, it can be prepared from these reactants. Surprisingly, the material of composition $C_2H_5NH_3CuCl_2\cdot C_2H_5NH_2$, a solid with a negligible dissociation pressure, was found to be an equimolar mixture of ethylammonium chloride and of the neutral 1:1 complex. All of the lines in its X-ray powder pattern were found to correspond to lines of $C_2H_5NH_3Cl$ or of $CuCl\cdot C_2H_5NH_2$, and all of the medium and strong lines of each of the latter substances were observed in the reaction product. This is in sharp contrast to the results in the diethylamine system.[3]

A number of the dichlorocuprate(I) complexes reported in this and previous[2,3] studies, though formulated as salts, have melting points below room temperature. Presumably, the lattice energies are low for steric reasons. This is similar to the case reported by Harris,[10] who observed that alkylammonium tetrafluoroborates absorbed boron trifluoride to give salts of the $B_2F_7^-$ anion, with greatly depressed melting points.

The results of this work are in accord with the previously discussed trend[3] that the major steric influence of the degree of alkyl substitution on nitrogen in aliphatic amine ligands is on the maximum coordination number, rather than on the stability of comparable complexes of lower coordination number.

---

[10] J. J. Harris, *Inorg. Chem.*, **5**, 1627 (1966).

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

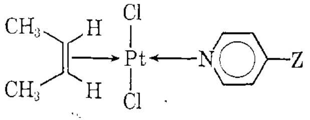
Contribution from the Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221

The Preparation and Infrared Spectra of Some *trans*-Dichloro-*cis*-2-butene-(4-Z-pyridine)- and -(4-Z-pyridine N-oxide)-Platinum(II) Complexes

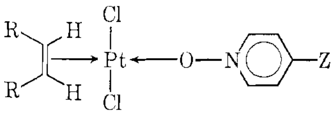
By Paul Schmidt and Milton Orchin

Received February 25, 1967

Previous work in this laboratory[1] purported to demonstrate the effect on the C=C stretching frequency of substituents Z of the pyridine N-oxide ligand in *trans*-dichloro-(4-Z-pyridine N-oxide)-ethyleneplatinum(II) complexes (**2**, R = H). A new series of *cis*-2-butene–platinum(II)–pyridine complexes, (*cis*-C_4H_8)Pt(4-Z-C_5H_4N)Cl_2 (**1**), has now been prepared, where Z is H, CH_3, $COCH_3$, CN, CH_2OH, and CH_3 (2,4,6-trimethyl), in order to study the effect of Z on the olefin stretching frequency. This stretching frequency was found to be essentially independent of the nature of Z. Part of the corresponding series of *cis*-2-butene–pyridine N-oxide complexes was also prepared and again the stretching frequencies were independent of Z. However, the pyridine ligands, even though more basic, resulted in higher olefin stretching frequencies than the pyridine N-oxides, suggesting that π^* orbitals of coordinated pyridine may compete with the olefin π^* orbital for metal d electrons. Reexamination of the spectra of the corresponding ethyleneplatinum(II)–pyridine N-oxide complexes shows that our previous report showing a correlation between the electronic character of Z and the ethylene stretching frequency may be in error because some bands assigned to ethylene are more appropriately assigned to the stretching frequencies of the N-oxide.



1



2

Experimental Section

New Compounds.—Most of the complexes were prepared either by the displacement of ethylene (method 1) from the corresponding ethylene–pyridine complexes (or ethylene–pyridine N-oxide complexes) or by splitting (method 2) the *cis*-2-butene platinous chloride dimer.[2] In the displacement reaction, liquid *cis*-2-butene was poured directly onto the solid ethylene complex in a reaction flask maintained at 0°. The flask was brought to room temperature with vigorous stirring. Repetition of this process was necessary for quantitative displacement of the ethylene. In the splitting synthesis, aqueous KCl was used to cleave the dimer. The appropriate substituted pyridine or pyridine N-oxide was then added to the water-soluble *cis*-2-butene salt and chloride displacement gave the insoluble yellow complex. A third synthesis (method 3) consisted of dissolving Zeise's salt, K[$C_2H_4PtCl_3$], in acetone and adding liquid *cis*-2-butene to the solution. After the excess olefin and acetone were evaporated, the *cis*-2-butene salt was dissolved in water and allowed to react with the pyridine or pyridine N-oxide in the manner described above. The substituted pyridines are commercially available; the substituted pyridine N-oxides were pre-

Table I

Properties of (*cis*-C_4H_8)Pt(L)Cl_2 Complexes

Z	Mp, °C	Anal, %				σ_p	$\nu_{C=C}$, cm^{-1}		
		Calcd		Found[a]					
		C	H	C	H		Mull	Pellet	$DCCl_3$
				4-Z-Pyridine Complexes (**1**)					
H[b]	122	26.94	3.27	26.95	3.17	0	1522		1528
CH_3[b]	108	28.92	3.64	28.80	3.52	−0.17[c]	1522		1528
$COCH_3$[b]	125	29.82	3.41	29.64	3.14	+0.52[c]	1522		1528
CN[b]	180 dec	28.18	2.84	28.21	3.06	+0.63[c]	1521	1521	1527
CH_2OH[d]	101	27.85	3.51	28.02	3.30	...	1523		1529
CH_3[d,e]	135	32.51	4.32	32.63	4.12	...	1523		1525
				4-Z-Pyridine N-Oxide Complexes (**2**, R = CH_3)					
H[f]	130 dec	25.90	3.14	25.84	3.11	0	1503	1502	
Cl[b]	156 dec	23.93	2.68	23.91	2.61	+0.22[c]	1506	1503	
$COOCH_3$[b]	126 dec	27.80	3.18	27.91	3.00	+0.31[g]	1503	1504	
CH_3[f]	122 dec	27.85	3.51	27.81	3.35	−0.17[c]	1506	1502	
CN[b]	143 dec	27.16	2.73	26.98	2.66	+0.63[c]	1504	1502	

[a] Galbraith Laboratories, Knoxville, Tenn. [b] Prepared by method 1. [c] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953). [d] Prepared by method 2. [e] This is 2,4,6-trimethylpyridine. [f] Prepared by method 3. [g] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 425 (1958).

---

(1) S. I. Shupack and M. Orchin, *J. Am. Chem. Soc.*, **85**, 902 (1963).

(2) H. B. Jonassen and W. B. Kirsch, *ibid.*, **79**, 1279 (1957).