Notes

Contribution from the Department of Chemistry,
Purdue University, Lafayette, Indiana 47907

The Redox Behavior of Rhenium Halides. III. The Reaction of Rhenium(III) Chloride with 2,2′-Bipyridyl: Characterization of the Reduction Products and a Reassessment of the Course of the Reaction[1]

By D. G. Tisley[2] and R. A. Walton*

Received January 19, 1971

From recent studies we have shown[3] that rhenium(III) chloride is capable of undergoing redox reactions with a variety of monodentate heterocyclic tertiary amines and furthermore that the products of such reactions retain the Re_3 cluster of the parent halide. With the realization that, like other metal halides of the early transition series,[4] rhenium(III) chloride can undergo reduction reactions with certain donor molecules we are able to explain the course of several reactions of this halide which have until now been little understood. In this report we describe our studies on the rhenium(III) chloride–2,2′-bipyridyl system which we believe is representative of the reactions of this halide with bidentate tertiary amines.

Experimental Section

Rhenium(III) chloride was prepared by the thermal decomposition of rhenium(V) chloride in a nitrogen stream and used without further purification. *Anal.* Calcd for $ReCl_3$: Re, 63.6; Cl, 36.4. Found: Re, 63.7; Cl, 35.9.

2,2′-Bipyridyl was recrystallized twice from petroleum ether (bp 30–60°). Acetone was B.D.H. Analytical Reagent grade and was stored over anhydrous calcium sulfate prior to use.

Carbon, hydrogen, and nitrogen analyses were performed by the University of Reading, U. K., microanalytical laboratory. Chlorine was determined gravimetrically and rhenium spectrophotometrically by the α-furildioxime method.

Electronic spectra were recorded on a Unicam 700c spectrophotometer equipped with diffuse-reflectance attachment and on a Cary 14 spectrophotometer. Infrared spectra in the region 4000–400 cm^{-1} were obtained with Perkin-Elmer 457 and Beckman IR 12 spectrophotometers. Conductivities were measured using a Pye 11700 conductance bridge and a Mullard conductivity cell. X-Ray powder data were obtained using a Philips camera (Debye–Scherrer type) and Cu $K\alpha$ radiation (λ 1.5418 Å) with an exposure time of 8 hr. Oxidation state analyses were carried out using a method based upon that of Noddack and Noddack.[5] The following procedure was found to be the most satisfactory. A weighed sample of the rhenium(III) chloride–2,2′-bipyridyl product was refluxed with an alkaline (NaOH) sodium chromate solution for 30 min with *constant stirring*. The mixture was then cooled, acidified (pH ∼2) with sulfuric acid, heated on a steam bath for 15 min, cooled, and filtered.[6] The filtrate was made alkaline (pH ∼9–10) with ammonia solution and reheated on a steam bath for a further 15 min. The precipitated chromium(III) hydroxide was filtered off and heated at 500° for 10 min, and the residue was weighed as Cr_2O_3.

$Re_3Cl_9(bipy)_{1.5}$.—The addition of a solution of 0.2 g of 2,2′-bipyridyl in 10 ml of acetone to a solution of 0.2 g of rhenium(III) chloride in 10 ml of acetone, both at room temperature, resulted in the rapid formation of a dark blue-purple precipitate. This was immediately filtered off, washed with acetone and diethyl ether, and dried in a vacuum desiccator over $CaCl_2$; yield 0.21 g. *Anal.* Calcd for $C_{15}H_{12}N_3Re_3Cl_9$: C, 16.2; H, 1.1; N, 3.8; Cl, 28.8; Re, 50.1. Found: C, 16.4; H, 1.3; N, 3.9; Cl, 28.7; Re, 50.3.

$Re_3Cl_9(bipy)_2$.—If, instead of filtering the above reaction mixture once precipitation was complete, the precipitate was left in contact with the 2,2′-bipyridyl solution for not less than 24 hr, an insoluble product containing a *higher* proportion of bipyridyl could be isolated. This compound was identical in appearance with $Re_3Cl_9(bipy)_{1.5}$ but analyzed closely for $Re_3Cl_9(bipy)_2$. *Anal.* Calcd for $C_{20}H_{16}N_4Re_3Cl_9$: C, 20.1; H, 1.6; N, 4.7; Cl, 26.8. Found: C, 19.8; H, 2.0; N, 4.8; Cl, 26.0.

Re_3Cl_9bipy.—A further preparation conducted at 0° and with the immediate filtration of the resulting precipitate afforded a dark blue-purple compound which contained a *lower* proportion of bipyridyl. *Anal.* Calcd for $C_{10}H_8N_2Re_3Cl_9$: C, 11.6; H, 0.8; N, 2.7; Cl, 30.9. Found: C, 11.8; H, 1.1; N, 2.9; Cl, 30.8.

$Re_3Cl_8(bipy)_2$.—An obvious extension to the above studies was to perform the reactions at higher temperatures; products previously formulated as Re_2Cl_4bipy[7] and $Re_3Cl_9(bipy)_2$[8] were both prepared from hot acetone solutions, so a higher proportion of bipyridyl was anticipated. Consequently, warm acetone solutions of the reactants were mixed and refluxed for 10 min before filtration. Again the product was a dark blue-purple precipitate, identical in appearance with those obtained previously. *Anal.* Calcd for $C_{20}H_{16}N_4Re_3Cl_8$: C, 20.8; H, 1.4; N, 4.8; Cl, 24.6; Re, 48.4. Found: C, 19.8; H, 1.7; N, 4.4; Cl, 24.3; Re, 49.7.

The stoichiometries of the products were very sensitive to the reaction conditions but, by using the conditions noted, products approximating to the formulations shown could be isolated. Heating the products at 100° under vacuum produced no sublimates of 2,2′-bipyridyl or 2,2′-bipyridinium chloride and no significant changes in the analytical figures.

$(bipyH)_2Re_3Cl_{11}$.—When any of the products from the above reactions were dissolved in a 4:1 v/v methanol–12 *M* hydrochloric acid mixture, in the absence of excess 2,2′-bipyridyl, a clear red solution was formed and this produced crops of dark red, needle-shaped crystals on slow evaporation. *Anal.* Calcd for $C_{20}H_{18}N_4Re_3Cl_{11}$: C, 19.0; H, 1.4; N, 4.4; Cl, 31.1. Found: C, 18.1; H, 1.7; N, 4.4; Cl, 31.5.

Results

Analytical data for the products isolated from the reaction of rhenium(III) chloride with 2,2′-bipyridyl in acetone showed conclusively that the Re:Cl ratio in the products approaches 1:3, at first sight implying that the Re_3Cl_9 cluster has not been disrupted. This bears out the result of an earlier study on this system in which we reported[8] the isolation of materials analyzing closely for $Re_3Cl_9(bipy)_{1.5}$ and $Re_3Cl_9(bipy)_2$. In the present work we have also isolated products of stoichiometry Re_3Cl_9bipy and $Re_3Cl_8(bipy)_2$ and can rule out the presence of the rhenium(II) species Re_2Cl_4bipy which was previously reported to be the principal reaction product.[7]

(a) **Electronic Spectra.**—A feature common to all compounds containing the trimeric rhenium cluster is

---

[1] This work was carried out in part at the University of Reading, U. K.

[2] Research Associate, 1970–1971.

[3] D. G. Tisley and R. A. Walton, *Inorg. Nucl. Chem. Lett.*, **6**, 479 (1970).

[4] R. A. Walton, *Progr. Inorg. Chem.*, in press.

[5] W. Noddack and I. Noddack, *Z. Anorg. Allg. Chem.*, **215**, 182 (1933).

[6] It was found essential to decompose these rhenium chloride derivatives in alkaline chromate solution as quickly as possible. If, instead, prolonged heating (12–20 hr) on a steam bath was employed, then this procedure often resulted in the precipitation of large quantities of *acid-insoluble* chromium species. The subsequent calculation of the rhenium oxidation state then gave ridiculous results.

[7] R. Colton, R. Levitus, and G. Wilkinson, *J. Chem. Soc.*, 4121 (1960).

[8] F. A. Cotton and R. A. Walton, *Inorg. Chem.*, **5**, 1802 (1966).

the presence of two absorption bands in the visible and near-infrared spectra in the regions 17,500–19,500 and 11,500–13,500 cm^{-1}; of these, that at higher energy is the more intense.[8–10] In addition, clusters in which the rhenium is in a formal oxidation state of 3+ have a weak band in the region 8000–8300 cm^{-1}, which appears to be diagnostic of the presence of the rhenium(III) trimeric cluster;[3] in all complexes of rhenium(III) chloride whose electronic spectra we have studied, and these include nitrogen, oxygen, and phosphorus donor complexes and complex anions such as $Re_3Cl_{11}^{2-}$, this low-energy band is always present. The diffuse reflectance spectra of the 2,2′-bipyridyl adducts which we have prepared were identical in the region 20,000–5000 cm^{-1}, exhibiting two bands: one, a broad band, at 17,800 cm^{-1} and the other at 11,200 cm^{-1}. The high-energy band was the more intense. This is consistent with the retention of the trimeric Re_3 cluster. However, since the band near 8000 cm^{-1} is absent, the cluster is no longer in the 3+ oxidation state. In addition, the positions of the two bands of the spectrum are shifted to slightly lower energies than are normally found with rhenium(III) cluster compounds—a phenomenon which has been observed with reduced cluster species of the type $Re_3Cl_6L_3$, where L = pyridine, β- or γ- picoline, or benzimidazole,[3] consistent with the presence of reduced rhenium halide species.

(b) **Conductivity Measurements.**—The rhenium(III) chloride–bipyridyl products were insoluble in nonpolar solvents but slightly soluble in polar solvents such as acetonitrile and dimethylformamide. Attempts were made to measure the conductivity of a 0.001 *M* solution of $Re_3Cl_9(bipy)_{1.5}$ in dimethylformamide. It was found that the conductivity of the solution increased with time, so that no conclusions could be reached as to electrolyte type. However, the molar conductance of the solution close to the time of its preparation was ~50 ohm^{-1} cm^{-2} and it is therefore probable that some ionic species are present.

(c) **Infrared Spectra, 4000–400 Cm^{-1}.**—The infrared spectra of all adducts were identical. In addition to the bands expected[11,12] for compounds containing coordinated 2,2′-bipyridyl, additional bands characteristic of the 2,2′-bipyridinium cation were observed, *viz.*, a strong band at 1528 cm^{-1} and weaker bands at 990 and 887 cm^{-1}. No absorption bands characteristic of ReO or ReOH moieties were observed. To check further that hydrolysis was not giving rise to the $bipyH^+$ species, we prepared a sample of $Re_3Cl_9(bipy)_{1.5}$ in a nitrogen atmosphere using rigorously dried solvent and reagents. The infrared spectrum of this product was identical with that of the other preparations.

(d) **Oxidation State Determinations.**—Using the alkaline chromate method outlined in the Experimental Section, the products which analyzed as $Re_3Cl_9(bipy)_{1.5}$ and $Re_3Cl_8(bipy)_2$ were found to have oxidation states of 2.65 and 2.38, respectively. To test the generality of this procedure the oxidation states of the following standard compounds of rhenium(II), -(III), and -(IV) were also determined: $[Re_3Cl_6(py)_3]_n$, 1.87; Re_3Cl_9, 3.05; $[n\text{-}Pr_4N]ReCl_5 \cdot H_2O$, 3.94.

(e) **X-Ray Powder Data.**—Both $Re_3Cl_9(bipy)_{1.5}$ and Re_3Cl_9bipy, the products which are formed under very mild reaction conditions, were amorphous to X-rays. However, $Re_3Cl_9(bipy)_2$ and $Re_3Cl_8(bipy)_2$, which are formed under rather more forcing reaction conditions, were at least partially crystalline although the powder lines were rather broad and diffuse. As far as we can judge there is a close similarity between the powder patterns of these two products implying that they are perhaps closely related phases; the *d* spacings (Å) are as follows: $Re_3Cl_9(bipy)_2$, 9.9 s, 8.5 s, 7.5 s, 6.4 m, 4.9 w; $Re_3Cl_8(bipy)_2$, 9.9 s, 8.4 s, 7.5 s, 6.4 s, 4.8 m, 2.1 w, 1.8 vw.

Discussion

In our study of the rhenium(III) chloride–2,2′-bipyridyl system, in which we have isolated products analyzing for Re_3Cl_9bipy, $Re_3Cl_9(bipy)_{1.5}$, $Re_3Cl_9(bipy)_2$, and $Re_3Cl_8(bipy)_2$, the varying compositions reflect the complexity of this reaction. The diffuse-reflectance spectra of these products provide strong evidence that although the Re_3 cluster is retained, reduction has occurred to below the 3+ oxidation state. The reaction of these derivatives with methanol–HCl and their resulting oxidation to yield the authentic rhenium(III) derivative, $(bipyH)_2Re_3Cl_{11}$, further confirms the presence of the Re_3 cluster. This latter reaction is typical of that shown by reduced rhenium chloride species of this type; *e.g.*, $Re_3Cl_6(py)_3$ is oxidized to $(pyH)_2Re_3Cl_{11}$.[3]

Since the infrared spectra of the reaction products were identical and conclusively show the presence of the 2,2′-bipyridinium cation in addition to 2,2′-bipyridyl, the formulation of these compounds is clearly not straightforward. The analytical data may indeed simply reflect the average composition of the products. What is clear is that the course of the above reactions is in keeping with our observations on the related reactions of rhenium(III) chloride with monodentate tertiary amines such as pyridine,[3] from which the reduced species $Re_3Cl_6L_3$ may be isolated. Since in the latter systems amine hydrochloride is an important by-product, it seems that in the reduction of rhenium(III) chloride by 2,2′-bipyridyl, any 2,2′-bipyridinium chloride which is initially formed reacts with the reduced rhenium chloride–bipyridyl phase to produce insoluble products such as $(bipyH)_xRe_3Cl_9(bipy)_y$, in which the formal oxidation state of the rhenium is $+(3 - x)$. For instance, the products analyzing as $Re_3Cl_9(bipy)_{1.5}$ and $Re_3Cl_8(bipy)_2$ which had oxidation states of ~2.65 and ~2.4, respectively, could accordingly be formulated as $(bipyH)_{1.05}Re_3Cl_9(bipy)_{0.45}$ and $(bipyH)_{0.8}Re_3Cl_8(bipy)_{1.2}$. The conductivity of a dimethylformamide solution of $Re_3Cl_9(bipy)_{1.5}$ is consistent with the above ionic formulation.

We believe that the redox reactions which we have observed for the rhenium(III) chloride–2,2′-bipyridyl system would also explain the related behavior of this halide toward 1,10-phenanthroline.[8] Thus, the purple insoluble products previously formulated as $Re_3Cl_9(phen)_x$, where x had values ranging from 2 to ~2.8,[8] are almost certainly reduced species of the general type $(phenH)_xRe_3Cl_9(phen)_y$. In addition, our work suggested that the materials analyzing for $Re_3Cl_9(terpy)_x$ where terpy = 2,2′,2′′-terpyridyl and x = 1, 1.33, or 2, which were recently reported by Fergusson

---

[9] F. A. Cotton and J. T. Mague, *Inorg. Chem.*, **3**, 1402 (1964).

[10] B. H. Robinson and J. E. Fergusson, *J. Chem. Soc.*, 5683 (1964).

[11] A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, **9**, 211 (1959).

[12] R. G. Inskeep, *ibid.*, **24**, 763 (1962).

and Hickford,[13] might also contain rhenium chloride species in oxidation states of less than 3+. Accordingly we prepared these derivatives according to the method of Fergusson and Hickford[13] and recorded their electronic and/or vibrational spectra. For all three products their infrared spectra (4000–400 cm^{-1}), recorded as Nujol mulls, revealed bands characteristic of the 2,2′,2″-terpyridinium cation[14] and 2,2′,2″-terpyridyl.

The mull electronic specta of the solids prepared by the method which were described as affording $Re_3Cl_9(terpy)_{1.33}$ and $Re_3Cl_9(terpy)_2$[13] did not show a low-energy absorption band near 8000 cm^{-1} and resembled closely the spectra of the reduced species isolated from the rhenium(III) chloride–2,2′-bipyridyl systems.

Acknowledgments.—This research was supported in part by the National Science Foundation (Grant GP-19422) and the Advanced Research Projects Agency (administered through the Purdue University Materials Science Council). We thank the S.R.C. for a maintenance grant to D. G. T. during the period while part of this work was carried out at the University of Reading.

[13] J. E. Fergusson and J. H. Hickford, *Inorg. Chim. Acta*, **2**, 475 (1968).

[14] In particular, a fairly intense band at 1540–1535 cm^{-1} is characteristic of the cation and is not shown in the spectra of complexes of 2,2′,2″-terpyridyl.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
NORTH CAROLINA STATE UNIVERSITY,
RALEIGH, NORTH CAROLINA 27607

Spin-Forbidden Transitions in Chromium-Sulfur Chelates

BY KEITH DEARMOND* AND WILLIAM J. MITCHELL

Received February 1, 1971

For the d^3 chromium system, crystal field theory predicts in O_h symmetry three low-energy spin-forbidden transitions, $^2E \leftarrow {}^4A_2$, $^2T_1 \leftarrow {}^4A_2$, and the $^2T_2 \leftarrow {}^4A_2$, all described in orbital notation as $t_2^3 \rightarrow t_2^3$ transitions. However, the small radiative probability of these transitions frequently precludes observing them in solution absorption spectra. Use of dilute single-crystal samples to obtain better resolution and increased absorbance is limited by the availability of transparent isomorphous host lattice materials. Polymer solvent media may provide a suitable compromise between liquid solution and solid solution determination of spin-forbidden transitions.

Reported below are the energies of these transitions in five tris chromium(III) complexes: diethyldithiophosphate, dtp; dimethyldithiocarbamate, dmtc; diethyl dithiocarbamate, detc; methyl xanthate, mxan; and ethyl xanthate, exan. The $^2T_2 \leftarrow {}^4A_2$ transition has not been previously located for these complexes. An explanation of the extra band in the region of the $^4T_1$ band for $Cr(dtp)_3$ is given. The emission spectra for the complexes are also reported, clarifying some earlier results.

Experimental Section

Synthesis.—The sulfur chelates were synthesized by literature methods.[1-3] Purity was determined by melting point, thin layer chromatography, and C-H analysis. Compounds were stored at 0° after purification and repurified just before use.

Glassy solvents used were EPA [ether–isopentane–ethanol (5:5:2)] and EPA–$CHCl_3$ (2:1). Polymer samples were made by dissolving the complexes in partially polmerized methyl methacrylate syrup. Further polymerization was done thermally (75° until firm and then 100° for 2 days). The samples were stored under vacuum until use.

The $Cr(dmtc)_3$ and $Cr(exan)_3$ crystals diluted into the corresponding indium host chelate were grown from reagent grade acetone. The $Cr(dtp)_3$–$In(dtp)_3$ crystals were obtained as flakes from 95% ethanol.

Results and Discussion

The absorption spectra of $Cr(mxan)_3$ and $Cr(exan)_3$ in polymer and crystalline hosts contain resolved weak bands at 18.1 and 18.4 kK and shoulders at 13.0 and 13.9 kK superimposed upon the $^4T_2 \leftarrow {}^4A_2$ transition. The lowest energy transition is assigned as the $^2E \leftarrow {}^4A_2$ transition consistent with the emission spectrum. The shoulder at 13.9 kK is tentatively assigned as the $^2T_1 \leftarrow {}^4A_2$ transition. On the basis of their sharpness, intensity, and the Sugano–Tanabe diagram, the two narrow resolved bands at 18.1 and 18.4 kK are assigned as the trigonally split components (^2E and $^2A_2$) of the $^2T_2$ state.

The emission from these complexes (Table I) is narrow ($\bar{\nu}_{1/2}$ = 0.410 kK) and overlaps with the $^2E \leftarrow {}^4A_2$ absorption band and therefore is assigned as a $^2E \leftarrow {}^4A_2$ *phosphorescence*.[4] The emission decay curve is exponential and gives a lifetime (Table I) consistent with this assignment.

TABLE I
77°K EMISSION MAXIMA (kK) AND LIFETIMES (μSEC)

	Crystal		Polymer[a]	
Compound	$\bar{\nu}$	τ	$\bar{\nu}$	τ
$Cr(dmtc)_3$	11.9	10[b]	12.5	128
$Cr(detc)_3$	11.9	34[b]	12.5	120
$Cr(maxn)_3$	12.5	50[c]	12.7	360
$Cr(exan)_3$	12.8	46[c]	12.7	350

[a] Unchanged in glassy solution. [b] Independent of concentration to 0.1% Cr^{3+}–$In(dmtc)_3$. [c] Independent of concentration to 0.1% Cr^{3+}–$In(exan)_3$.

The 83°K absorption spectrum for the $Cr(dmtc)_3$ dilute crystal and polymer samples indicates weak spin-forbidden absorption bands at 12.7, 13.0, 14.0, 18.3, and 18.6 kK. In glassy solution the bands at 12.7, 13.0, and 14.0 were not observed. By analogy to the xanthates the bands at 12.7 and 14.0 kK are assigned as the $^2E \leftarrow {}^4A_2$ and $^2T_1 \leftarrow {}^4A_2$ transitions, respectively. In like manner the transitions observed at 18.3 and 18.6 kK are assigned as the trigonally split components of the $^2T_2 \leftarrow {}^4A_2$ transiton.

The emission maximum for $Cr(dmtc)_3$ and $Cr(detc)_3$ (Table I) shows a small Stokes shift, but the lifetime (Table I) is 10–15 times greater than usually observed for the Cr(III) fluorescence ($^4T_2 \rightarrow {}^4A_2$).[5] Further the emission half-width (0.80 kK) is much too narrow for

---

[1] C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

[2] F. Galsbol and C. E. Schaffer, *Inorg. Syn.*, **10**, 42 (1968).

[3] D. E. Coldbery, W. C. Fernelius, and M. Shamma, *ibid.*, **6**, 142 (1960).

[4] P. Cancellieri, E. Cervone, C. Furlani, and G. Sartori, *Z. Phys. Chem. (Frankfurt am Main)*, **62**, 35 (1968).

[5] G. B. Porter and S. Chen, *J. Amer. Chem. Soc.*, **92**, 2189 (1970).