Inorganica Chimica Acta, 14 (1975) L45 - L46

Complex Halides of the Transition Metals. Part XIX.[1] Some Remarks Concerning the Electronic Absorption Spectra of the $[Re_2Cl_8]^{3-}$ and $[Re_2Cl_8]^{4-}$ Anions

J. R. EBNER and R. A. WALTON

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, U.S.A.

(Received May 28, 1975)

Our attention has been drawn to a paper[2] which recently reported the electronic absorption spectrum of a solution which was purported to contain the species $[Re_2Cl_8]^{n-}$ (n = 3 or 4). We feel that this spectral result merits further comment.

Earlier studies on the polarographic reduction of acetonitrile solutions of the $[Re_2Cl_8]^{2-}$ anion[3] led us to propose that both the $[Re_2Cl_8]^{3-}$ and $[Re_2Cl_8]^{4-}$ anions were generated. This system has recently been subjected to fairly detailed reinvestigation following more extensive electrochemical studies.[2,4] While there is little doubt that the $[Re_2Cl_8]^{3-}$ anion is indeed formed, the full characterization of this species has proved to be rather difficult. Thus, efforts to isolate salts of the $[Re_2Cl_8]^{3-}$ and $[Re_2Cl_8]^{4-}$ anions have not yet been successful and attempts to measure the esr spectra of frozen solutions of $[Re_2Cl_8]^{3-}$ were thwarted by the short lifetime of this species.[4]

We recently isolated[1,5] several tertiary phosphine derivatives of the $[Re_2Cl_8]^{3-}$ and $[Re_2Cl_8]^{4-}$ anions. These complexes, which are of stoichiometry $Re_2Cl_5(PRPh_2)_3$, where R = Me or Et, and $Re_2Cl_4(PR_3)_4$, where PR_3 = PMe_3, PEt_3, PPr^n_3, PMe_2Ph or PEt_2Ph exhibit the structural characteristics which have been predicted for species derived by the one- or two-electron reductions of $[Re_2Cl_8]^{2-}$.[6]

In the electronic absorption spectra of these complexes, we noted[1] the absence of the intense absorption at ~ 700 nm which is characteristic of the $[Re_2Cl_8]^{2-}$ anion and its derivatives (*e.g.* $Re_2Cl_6(PR_3)_2$).[7-9] In addition, a very intense low energy absorption band is present in the *near infrared region* at ~ 1400 nm ($\epsilon > 2000$) in the spectra of paramagnetic $Re_2X_5(PRPh_2)_3$ (X = Cl or Br). This spectral feature is characteristic of the solid state complexes and their solutions in a variety of non-aqueous solvents. For a 1,2-dichloroethane solution of $Re_2Cl_5(PEtPh_2)_3$, the absorption at 1370 nm (ϵ = 2588) obeys Beer's Law over the concentration range 5×10^{-4} *M* - 5×10^{-5} *M*. While a definitive assignment for this band must await more detailed studies, including single crystal polarization measurements, we believe that this spectral feature is diagnostic of the presence of these and similar paramagnetic species.* Thus, Glinkina *et al.*[10] report that the $[Tc_2Cl_8]^{3-}$ anion, which is isoelectronic with $[Re_2Cl_8]^{3-}$, exhibits a fairly intense electronic absorption band ($\epsilon \sim 500$) between 1500 and 1700 nm.** Although these authors did not attempt an assignment of this band, we suggest that its origin is similar to that of the corresponding low energy absorption in the structurally related complexes $Re_2Cl_5(PRPh_2)_3$.

A similar feature is observed in the related spectra of the two-electron reduced products $Re_2X_4(PR_3)_4$, but in this instance it arises from *oxidation* of these complexes. Solutions of these derivatives prepared under rigorous oxygen-free conditions do not exhibit this absorption band, but when they are exposed to the atmosphere a band rapidly grows in at ~ 1380 nm. Of relevance to these spectral changes is the observation that the spectrum (350 - 1500 nm) of $Re_2Br_4(PEt_3)_4$ after oxidation is strikingly similar to that of $Re_2Br_5(PEtPh_2)_3$. Also, freshly prepared solutions of $Re_2X_4(PR_3)_4$ are gray in color, but change to green-yellow upon oxidation. The species $[Re_2Cl_4(PEt_3)_4]^+$, which can be generated by the electrochemical oxidation of $Re_2Cl_4(PEt_3)_4$,[11] is likewise a green-yellow color in solution. At the present time, the available evidence supports the oxidation product being $Re_2X_5(PR_3)_3$, $[Re_2X_4(PR_3)_4]^+$ or some structurally related species.

On the basis of our spectral studies on $Re_2X_4(PR_3)_4$ and $Re_2X_5(PRPh_2)_3$ there is no convincing

---

*Other rhenium halide phosphine complexes, such as $[ReCl_3(dppe)]_2$ and $[ReCl_3(dppm)]_n$, where dppe = $Ph_2PCH_2CH_2PPh_2$ and dppm = $Ph_2PCH_2PPh_2$, exhibit electronic absorption bands in the near infrared region (J. A. Jaecker, D. P. Murtha and R. A. Walton, *Inorg. Chim. Acta, 13,* 21 (1975) and J. R. Ebner, D. R. Tyler and R. A. Walton, *Inorg. Chem.*, to be submitted). However, these spectra are otherwise quite different from those of $Re_2Cl_5(PRPh_2)_3$.

**The paper by Glinkina *et al.*[10] erroneously reports the isolation of complexes of composition $M^I_8[Tc_2Cl_8]_3 \cdot 4H_2O$. These materials are in fact the salts $M^I_3[Tc_2Cl_8] \cdot 2H_2O$ (F.A. Cotton and L. W. Shive, *Inorg. Chem.*, to be published).

evidence that the electronic absorption spectrum of an acetonitrile solution of $[Re_2Cl_8]^{2-}$, measured after polarographic reduction,[2] is characteristic of either $[Re_2Cl_8]^{3-}$ or $[Re_2Cl_8]^{4-}$. The spectral range monitored (240 - 700 nm) did not extend into the near infrared region. In addition, from the work of Cotton and Pedersen[4] it is apparent that the low concentrations of $[Re_2Cl_8]^{3-}$ which can be generated at room temperature, together with its short lifetime (it decomposes by oxidation to an unknown species) makes its spectroscopic characterization rather difficult. All that can be concluded from the reported spectrum[2] is that it shows the presence of considerable amounts of unreduced $[Re_2Cl_8]^{2-}$.

On the basis of the foregoing discussion, it would be of interest to investigate the electronic absorption spectra of the paramagnetic species $[Re_2(C_6H_5COO)_4]^+$ and $[Re_2Cl_4(PEt_3)_4]^+$, both of which can be generated electrochemically.[11] Since they presumably exhibit a close structural relationship to $[Re_2Cl_8]^{3-}$ and $Re_2Cl_5(PRPh_2)_3$, we would predict the existence of an absorption band in the neighborhood of 1400 nm.

Acknowledgements

This work was supported by grants from the National Science Foundation (GP-43021X) and the Camille and Henry Dreyfus Foundation. We acknowledge some very useful discussions with Professor H. B. Gray. In particular, we wish to mention that Professor Gray first drew our attention to the facile oxidation of the complexes $Re_2X_4(PR_3)_4$. This observation was the result of collaborative spectral studies carried out in his laboratory by Mr. W. Trogler.

References

1 Part XVIII. J. R. Ebner and R. A. Walton, *Inorg. Chem., 14,* (1975) in press.
2 R. R. Hendriksma and H. P. van Leeuwen, *Electrochim. Acta, 18,* 39 (1973).
3 F. A. Cotton, W. R. Robinson and R. A. Walton, *Inorg. Chem., 6,* 1257 (1967).
4 F. A. Cotton and E. Pedersen, *Inorg. Chem., 14,* 383 (1975).
5 F. A. Cotton, B. A. Frenz, J. R. Ebner and R. A. Walton, *J. Chem. Soc., Chem. Comm.,* 4 (1974).
6 F. A. Cotton, *Accts. Chem. Res., 2,* 240 (1969).
7 F. A. Cotton, W. R. Robinson and R. A. Walton, *Inorg. Chem., 6,* 223 (1967).
8 F. A. Cotton, *Inorg. Chem., 4,* 334 (1965).
9 C. D. Cowman and H. B. Gray, *J. Am. Chem. Soc., 95,* 8177 (1973).
10 M. I. Glinkina, A. F. Kuzina and V. I. Spitsyn, *Russ. J. Inorg. Chem., 18,* 210 (1973).
11 F. A. Cotton and E. Pedersen, *J. Am. Chem. Soc., 97,* 303 (1975).