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Notes

An Unprecedented Monomeric Rhenium(V) Complex of the Ligand 1,4,8,11-Tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane

Md. Athar Masood and Derek J. Hodgson*

Department of Chemistry, University of Wyoming,
Laramie, Wyoming 82071-3838

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Introduction

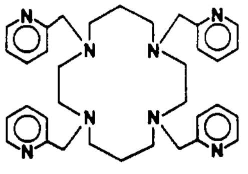
While rhenium is the heavy congener of manganese, the chemistries of the two elements are very different.[1-3] An important feature of the chemistry of rhenium is the existence of large number of easily accessible oxidation states which interconvert under mild redox conditions; from a synthetic viewpoint, this versatility allows the metal to coordinate to complex ligands in a variety of ways, leading to mixtures of products, whose separation and identification are often tedious. Another key feature is its ability to form strong multiple bonds to oxygen and nitrogen in the higher oxidation states [*e.g.* Re(IV)].

In many senses, the most accessible oxidation state of rhenium is Re(VII), which is obtained by mild oxidation of the metal. Re(V) is also accessible for oxo, nitrido, and imido complexes like $[ReOCl_3(PR)_2]$ and $[Re(NR)(PR_3)_2]$, which are also synthons for variety of reactions and are important synthetic and catalytic intermediates.[4,5] But only very recently was it demonstrated that a d^2 rhenium(V) center multiply bonded to a heteroatom such as oxygen or nitrogen has novel physical, chemical, and/or photophysical properties.[6,7] While some complexes of rhenium with substituted pyridines and substituted phosphines have been reported,[8] no cationic complexes with multidentate chelate ligands containing moieties like pyridines and bipyridines are known.

In our quest for a highly stabilized cationic Re(V) complexes, we felt that appropriate reactants were the neutral Re(V) *trans*-mer-$[Re(NPh)Cl_3(PPh_3)_2]$[9] complex and the sterically accommodating and novel ligand 1,4,8,11-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (L).[10] Here we report the synthesis and properties of the rhenium(V) complex $[Re(L)(NPh)(C_2H_5OH)](PF_6)_3$.

Experimental Section

Synthesis of $[Re(L)(NPh)(C_2H_5OH)](PF_6)_3$. All reagents were purchased from Aldrich Chemical Co. Solvents were dried according to standard literature procedures. The ligand L was synthesized by the procedure described in ref 10.



L

To a 250-mL three-neck round-bottomed flask containing 150 mL of thoroughly degassed absolute ethanol and the ligand (250 mg, 0.66 mmol) was added *trans-mer*-$[Re(NPh)Cl_3(PPh_3)_2]$ (136 mg, 0.15 mmol) under argon. The solution mixture was then heated to reflux, causing the initial green suspension to dissolve and the color of the resulting homogenized solution to turn violet-brown. The reaction mixture was refluxed for 48 h, cooled, and filtered, the filtrate was collected, and the solvent was removed by rotary evaporation. The solid residue was then loaded onto a neutral alumina column and eluted first with 1:1 v/v dichloromethane/hexane; this first fraction contained the unreacted ligand. It was then eluted with ethanol, and the purple-violet band was collected. The ethanol was then removed by rotary evaporation until the volume was reduced to 5 mL. To this was added 300 mg of NH_4PF_6 dissolved in 5 mL of ethanol to immediately give a crimson-violet, solid which was filtered off and washed with 5 mL of ethanol and 25 mL of diethyl ether to give 150 mg of the compound. Anal. Calcd for $ReC_{42}H_{55}F_{18}N_9OP_3$: C, 38.13; H, 4.19; N, 9.53. Found: C, 37.75; H, 4.22; N, 9.75.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer. Magnetic susceptibility was determined at 22 °C on a Johnson Matthey magnetic susceptibility balance; $HgCo(SCN)_4$ was used as calibrant. ^1H NMR spectra were recorded on a JEOL 270 spectrometer. Electronic spectra were obtained by using 1×10^{-3} mol dm^{-3} solutions in acetonitrile on a Perkin-Elmer Lambda 9 spectrometer. Cyclic voltammograms were obtained with a BAS 100A electrochemical analyzer. A three-electrode cell comprising a Pt button working electrode, a Pt wire auxiliary electrode, and a Ag/AgCl reference electrode was used. Solutions of the complex (1×10^{-3} mol dm^{-3}) in acetonitrile were used. The supporting electrolyte was 0.1 mol dm^{-3} tetraethylammonium perchlorate. All experiments were performed under a blanket of dry nitrogen at 22 ± 1 °C. All potentials are referred to Ag/AgCl.

X-ray Structure Determination. A crystal of dimensions $0.72 \times 0.40 \times 0.60$ mm^3 was mounted, and the structure was determined at 22 °C (295 K) on a Nicolet R3m/V diffractometer equipped with a molybdenum tube [$\lambda(K\alpha_1) = 0.709\,26$ Å; $\lambda(K\alpha_2) = 0.713\,54$ Å] and graphite monochromator. The structure was solved by direct methods and refined by least-squares techniques, the programs being from the SHELXTL IRIS system. The data were collected in the ranges $0° \le h \le 12°$, $0° \le k \le 22°$, $0° \le l \le 29°$ and were corrected for Lorentz–polarization and absorption effects. All hydrogen atoms were placed in fixed calculated positions (C–H = 0.96 Å) with isotropic thermal parameters determined by the heavy atoms to which they are bonded, while all the other atoms were refined anisotropically. Final values of the conventional R factors are $R = 0.0469$ and $R_w = 0.0553$ based on 2735 independent data with $I > 3\sigma(I)$.

Results and Discussion

The structure of the complex is unprecedented. In all previously reported complexes of this ligand, the coordination is either through the four aza nitrogen atoms of the tetraazacyclotetradecane ring[11] or (in the case of ruthenium) through three of the aza nitrogen atoms and three pyridyl nitrogen atoms.[12] In addition, there are examples in which all four of the aza nitrogen

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(1) Fergusson, J. E. *Coord. Chem. Rev.* **1966,** *1,* 459.

(2) (a) Ruffs, C. L. *Crit. Rev. Anal. Chem.* **1970,** *1,* 335. (b) Borisova, L. V.; Ermakov, A. N. *Tr. Vses. Soveshch. Probl. Reniya, 3rd* **1968,** *1,* 123; *Chem. Abstr.* **1971,** *74,* 119545z.

(3) (a) Ryashentseva, M. A.; Minachev, K. M. *Russ. Chem. Rev. (Engl. Transl.)* **1969,** *38,* 944. (b) Broadbent, H. S. *Ann. N.Y. Acad. Sci.* **1967,** *58,* 145. (c) Rouschias, G. *Chem. Rev.* **1974,** *74,* 531.

(4) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980,** *31,* 123.

(5) Chisholm, M. H.; Rothwell, I. P. *Comprehensive Coordination Chemistry*; Pergamon: Oxford, U.K., 1987; Vol. 2, Chapter 13.4.

(6) Thorp, H. H.; Van Houten, J.; Gray, H. B. *Inorg. Chem.* **1989,** *28,* 889.

(7) Neyhart, G. A.; Bakir, M.; Boaz, J.; Vining, W. J.; Sullivan, B. P. *Coord. Chem. Rev.* **1991,** *111,* 27.

(8) Bartley, S. L.; Dunbar, K. R.; Shih, K. Y.; Fanwick, P. E.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1993,** 98.

(9) La Monica, G.; Cenini, S. *Inorg. Chim. Acta* **1978,** *29,* 183.

(10) Alcock, N. W.; Balakrishnan, K. P.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1986,** 1743.

(11) (a) Wagner, F.; Mocella, M. T.; Aniello, M. J. D., Jr.; Wang, A. H.-J.; Barefield, E. K. *J. Am. Chem. Soc.* **1974,** *96,* 2625. (b) Blake, A. J.; Reid, G.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1988,** 1561. (c) Addison, A. W.; Sinn, E. *Inorg. Chem.* **1983,** *22,* 1225. (d) Walker, D. D.; Taube, H. *Inorg. Chem.* **1981,** *20,* 2828.

(12) Che Che, C.-M.; Tang, W.-T.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1988,** 2879.

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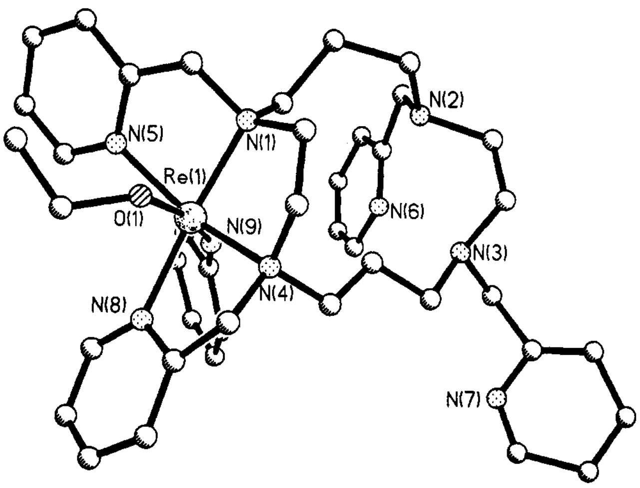

Figure 1. View of the complex cation $[Re(L)(NPh)(EtOH)]^{3+}$ in the crystals of the hexafluorophosphate salt. Hydrogen atoms are omitted for clarity.

atoms and all four pyridyl nitrogen atoms are involved in coordination, but these complexes are binuclear and the ligand is acting as donor to both metal centers.[10] In all of the previous monomeric systems, the metal is found in an encapsulated position within the substituted cyclam ring. In the present case, however, as is seen in Figure 1, the metal is located outside the substituted cyclam ring.

The formulation of the complex as a diamagnetic d^2 Re(V) rather than a paramagnetic d^1 Re(VI) complex is unquestionable. First, the room-temperature magnetic susceptibility measurement shows the complex to be diamagnetic. Additionally, the NMR spectrum exhibits a series of well-resolved peaks indicative of a diamagnetic species. Moreover, the EPR spectrum does not display any signals suggestive of a paramagnetic d^1 configuration.[13] Since the complex ion has an overall charge of +3, however, it must be deduced either that the ligand *trans* to NPh is ethanol rather than ethoxide or that one of the aza or pyridyl nitrogen atoms must be protonated. Regrettably, infrared spectroscopy is inconclusive. Similarly, ^{1}H NMR spectroscopy in a variety of solvents does not reveal the presence of either an OH or an NH proton. Neither the oxygen atom nor the uncoordinated nitrogen atoms participate in any intra- or intermolecular hydrogen bonding as donors or as acceptors. We are unable to identify, on the basis of the crystallographic structural data, that any nitrogen atom is protonated, and while it may be that we are seeing the averaged value of more than one tautomeric form, it is more probable that the *trans* ligand is EtOH rather than EtO^-. It must be noted, however, that the Re–O bond length *trans* to the Re═NPh linkage is 1.897(16) Å, which is similar to values previously reported for Re–O(ethoxide) bonds;[14] an Re(V)–O(ethanol) linkage would be predicted to be longer than these values.

Since the proton could not be located in the structural analysis, we cannot make a positive conclusion as to which tautomer (or tautomers) may be present. Simple basicity considerations clearly favor the formulation of the ligands as (neutral) L and EtOH rather than LH^+ and EtO^-, and we have assumed this formulation throughout this paper.

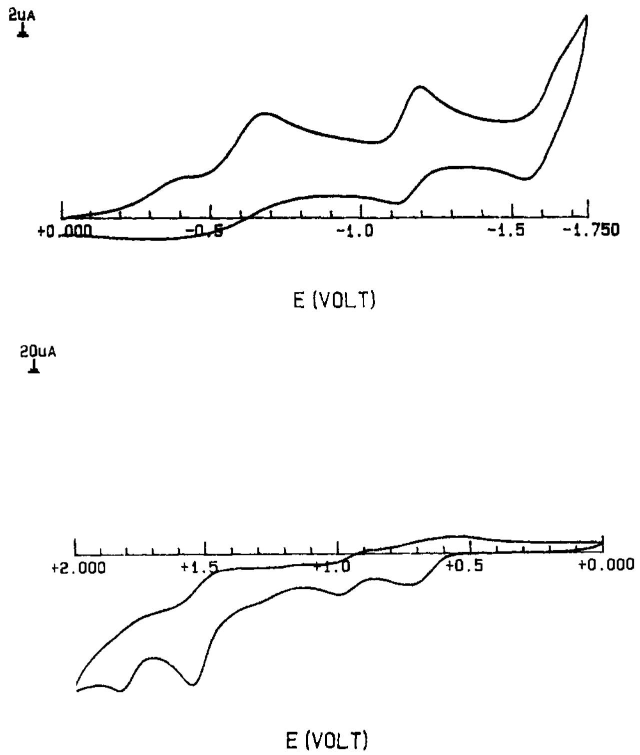

Figure 2. Cyclic voltammograms of the complex $[Re(L)(NPh)(EtOH)](PF_6)_3$ in acetonitrile with 0.1 M tetraethylammonium perchlorate as a supporting electrolyte (Pt button working electrode, Pt wire auxiliary electrode, and Ag/AgCl reference electrode).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg)

Re(1)–N(1)	2.138(14)	Re(1)–N(4)	2.131(16)
Re(1)–N(5)	2.154(18)	Re(1)–N(8)	2.141(13)
Re(1)–N(9)	1.703(16)	Re(1)–O(1)	1.897(13)
N(1)–Re(1)–N(4)	87.0(6)	N(1)–Re(1)–N(5)	78.0(7)
N(4)–Re(1)–N(5)	158.9(7)	N(1)–Re(1)–N(8)	163.2(6)
N(4)–Re(1)–N(8)	79.5(6)	N(5)–Re(1)–N(8)	112.2(6)
N(1)–Re(1)–N(9)	105.1(7)	N(4)–Re(1)–N(9)	106.5(7)
N(5)–Re(1)–N(9)	91.8(7)	N(8)–Re(1)–N(9)	88.3(6)
N(1)–Re(1)–O(1)	86.5(6)	N(4)–Re(1)–O(1)	82.4(6)
N(5)–Re(1)–O(1)	82.0(6)	N(8)–Re(1)–O(1)	82.0(5)
N(9)–Re(1)–O(1)	165.5(7)	Re(1)–O(1)–C(41)	135.3(12)
O(1)–C(41)–C(42)	108.8(26)		

The rhenium atom adopts a distorted octahedral geometry, with two cyclam nitrogen atoms [N(1) and N(4)] and two pyridyl nitrogen atoms [N(5) and N(8)] forming the equatorial "plane" while the axial ligands are the nitrogen atom from the phenylimido group [N(9)] and the oxygen atom of the coordinated ethanol [O(1)]. The extent of the distortion is evident from an examination of the *cis* bond angles at the metal, which vary from a minimum of 78.1° [N(1)–Re–N(5)] to a maximum of 106.6° [N(4)–Re–N(9)]. The mean deviation from the four-atom least-squares plane N(1), N(4), N(5), N(8) is 0.042 Å with one of the cyclam nitrogen atoms [N(1)] and one pyridyl atom [N(8)] lying 0.046 and 0.038 Å, respectively, above the plane while N(4) and N(5) lie 0.066 and 0.038 Å, respectively, below the plane. The rhenium atom is displaced 0.260 Å above the plane, on the same side as N(1). All of the uncoordinated nitrogen atoms [N(2), N(3), N(6), N(7)] are also located well above the plane, at distances ranging from 3.365 to 5.756 Å. As is evident from Figure 1, the central part of the ligand, the cyclam moiety, is in the saddlelike conformation. As a result of the lack of coordination at N(2) and N(3), the torsion angles around the nominally single C–C bonds adjacent to these atoms are very unusual; for example, the torsion angle N(4)–C(8)–C(7)–C(6) around the C(7)–C(8) bond is 178.6°.

The Re–N(9) bond length of 1.705(16) Å, which is approximately 0.035 Å shorter than the Re═NPh bond length of 1.740(6) Å found in the recently reported *trans*-$[Re(NPh)(bpy)_2(OEt)]^{2+}$ complex,[14a] is indicative (at least) of an extremely strong rhenium–nitrogen double bond. The present metal to imido bond length is the shortest with which we are familiar; for comparison,

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[13] Brewer, J. C.; Thorp, H. H.; Slagle, K. M.; Brudvig, G. W.; Gray, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 3171.

[14] (a) Bakir, M.; Paulson, S.; Goodson, P. A.; Sullivan, B. P. *Inorg. Chem.* **1992**, *31*, 1129. (b) Ciani, G. F.; D'Alfonso, G.; Romiti, P. F.; Sironi, A.; Freni, M. *Inorg. Chim. Acta* **1983**, *72*, 29. (c) Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1983**, *22*, 157.

in *trans-mer*-[Re(NPh)$Cl_3(PPh_3)_2$] the Re═N distance is 1.726(6) Å.[15] The Re–N(cyclam) bond lengths are similar to those in *trans*-[Re$(O)_2$(cyclam)]$^+$.[11b] Selected bond lengths and angles are presented in Table 1.

As is commonly seen in structures of this kind, the geometries of the PF_6^- anions are relatively poorly determined as the result of some crystallographic disorder in these ions. This problem is particularly apparent at P(3), where one nominally *trans* angle refines to a value of only 163°.

The electronic spectrum recorded in acetonitrile exhibited peaks at 719 nm (120 M^{-1} cm^{-1}) and 521 nm (250 M^{-1} cm^{-1}) in the visible region and bands at 322 nm (10 150 M^{-1} cm^{-1}) with shoulders at 350 nm (6320 M^{-1} cm^{-1}) and 255 nm (26 000 M^{-1} cm^{-1}) in the UV region. The low extinction coefficients suggest very little metal-to-ligand charge-transfer interactions.

The redox chemistry is rich but complicated. As can be seen from an examination of Figure 2, cyclic voltammetry in acetonitrile exhibits a series of reduction and oxidation peaks. The peak at $E_{1/2} = -1.17$ V with cathodic peak centered at −1.20 V and anodic peak centered at −1.14 V with $\Delta E_p = 60$ mV is clearly a reversible peak, but since it is preceded by two irreversible reductive processes, it appears probable that some structural change has taken place at less negative potentials. Electrochemical reversibility was also observed for the rhenium(V) complexes *trans*-[Re(NPh)(dppe)Cl]$^{2+}$ and *trans*-[Re(NPh)$(bpy)_2$(OEt)]$^{2+}$,[14a] where it is ascribed to the Re(V) ↔ Re(IV) couple, but the peak for the present complex is at much more negative potential than for these other complexes. As can be seen from an examination of Figure 2, bottom, a series of irreversible oxidation peaks is observed in the range +0.7 to +1.83 V. It is entirely possible that one of these represents a Re(VI) ↔ Re(VII) oxidation, but the irreversibility of the waves suggests that some chemical transformation may again be taking place.

In conclusion, we have obtained a stabilized Re(V) cationic species involving a multidentate, sterically constrained, chelate ligand; the resulting complex ion exhibits an unusual structure in which the metal is trapped by two aza and two pyridyl nitrogen atoms, while the other two aza and pyridyl nitrogen atoms are uncoordinated. Attempts to coordinate other transition metals [Ni(II), Cu(II)] to the free nitrogen atoms of the complex, to produce a bimetallic species, have proven unsuccessful.

Acknowledgment. This work was supported by the National Science Foundation through Grant No. CHE-9007607.

Supplementary Material Available: Summary of X-ray analysis (Table S1), atomic coordinates (Table S2), bond distances (Table S3) and angles (Table S4), hydrogen atom coordinates (Table S5), and anisotropic thermal parameters (Table S6) (14 pages). Ordering information is given on any current masthead page. Listings of observed and calculated structures factors for the complex are available from D.J.H. on request.

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[15] Forsellini, E.; Casellato, U.; Graziani, R.; Carletti, M. C.; Magon, L. *Acta Crystallogr.* **1984**, *C40*, 1795.