Inorg. Chem. **1992**, *31*, 2595–2598 **2595**

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Formation of the *trans*-[ReO$_2$]$^+$ Group from the Reactions of ReNCl$_2$(PPh$_3$)$_2$, ReCl$_4$(PPh$_3$)$_2$, and ReCl$_3$(CH$_3$CN)(PPh$_3$)$_2$ with Chelating Amines and Tetraazamacrocycles. Crystal Structure of *trans*-[ReO$_2$(cyclam)](PF$_6$) (cyclam = 1,4,8,11-Tetraazacyclotetradecane)

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Received August 27, 1991

The complexes ReNCl$_2$(PPh$_3$)$_2$ (**1**), ReCl$_4$(PPh$_3$)$_2$ (**2**), and ReCl$_3$(CH$_3$CN)(PPh$_3$)$_2$ (**3**) react with bidentate (L^2) and tetradentate (L^1) chelating amines and with 1,4,8,11-tetraazacyclotetradecane (cyclam) at room temperature, to afford cationic *trans*-dioxorhenium(V) complexes of the type [ReO$_2$(L^n)$_n$]$^+$ ($n = 1, 2$) and [ReO$_2$(cyclam)]$^+$ (**4**). These reactions constitute an unexpected alternative route to the synthesis of rhenium(V) complexes containing the *trans*-[ReO$_2$]$^+$ group. The complex cation **4** was isolated with three different counterions (ReO$_4^-$, Cl$^-$, PF$_6^-$). The perrhenate and chloride salts, **4**(ReO$_4$) and **4**(Cl), show a *single* infrared absorption at 772 cm^{-1}, assigned to the asymmetric stretching vibration of the *trans*-[ReO$_2$]$^+$ group, while the hexafluorophosphate salt, **4**(PF$_6$), shows *two* absorptions at 809 and 776 cm^{-1}, assigned to the same vibration. This fact has been attributed to the presence of *two* symmetry-inequivalent molecules of the cation **4** in the solid-state structure of **4**(PF$_6$), which has been determined by X-ray crystallography. Complex cation **4** is monomeric and has an approximately octahedral arrangement of ligands around the rhenium atom. The crystal structure consists of two independent cations and anions, and each ion has a crystallographically imposed symmetry center. **4**(PF$_6$) crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a = 5.533$ (1) Å, $b = 11.899$ (3) Å, $c = 13.622$ (3) Å, $V = 853.2$ (4) Å^3, $Z = 2$, $R = 0.063$, and $R_w = 0.081$ for 3006 observed reflections.

Recently, we reported the synthesis of a new class of monocationic, octahedral technetium(V) nitrido complexes with chelating amines[2] and tetraazamacrocycles[3] as a part of our current effort to prepare useful ^{99m}Tc myocardial diagnostic agents containing the Tc≡N group.[4] These compounds have been obtained by simple substitution reactions on the starting complex TcNCl$_2$(PPh$_3$)$_2$. Since, in the last years, radioisotopes of the β-emitting nuclides ^{186}Re ($\beta^- = 1.07$ MeV, $t_{1/2} = 90$ h) and ^{188}Re (2.12 MeV, $t_{1/2} = 17$ h) have been proposed as suitable candidates for therapeutic applications,[5] we decided to extend the study of the chemistry of chelating amines and tetraazamacrocyclic ligands to include their reactions with the analogous complex ReNCl$_2$(PPh$_3$)$_2$ containing the [Re≡N]$^{2+}$ group. In developing this chemistry, however, we failed to prepare analogous monocationic, octahedral rhenium(V) nitrido complexes, but we found that, under mild conditions, the Re≡N group was always lost and substituted by the *trans*-dioxo [O=Re=O]$^+$ group. This result appeared somewhat unexpected considering the relative stability of the [Re≡N]$^{2+}$ core. Previously, the enhanced reactivity of the rhenium(V) mixed halogen–phosphine complexes ReOCl$_3$(PPh$_3$)$_2$[6] and *cis*-ReO$_2$I(PPh$_3$)$_2$[7] toward amines and pyridine ligands had been reported. These facts led us to further investigate the change in the reactivity of mixed halogen–phosphine rhenium complexes toward chelating amines and tetraazamacrocycles upon variation of the metal oxidation state. We report here the reactions of the complexes ReNCl$_2$(PPh$_3$)$_2$ (**1**), ReCl$_4$(PPh$_3$)$_2$ (**2**), and ReCl$_3$(CH$_3$CN)(PPh$_3$)$_2$ (**3**) with these types of ligands, showing that the *trans*-[ReO$_2$]$^+$ group invariably forms, at room temperature, to produce cationic rhenium(V) complexes. These reactions, therefore, may consitute an alternative route to the synthesis of *trans*-dioxorhenium(V) complexes with open and cyclic amine ligands. The crystal structure of the complex [ReO$_2$(cyclam)](PF$_6$) (cyclam = 1,4,8,11-tetraazacyclotetradecane) will be also reported.

Experimental Section

Materials. All chemicals were of reagent grade and were used without further purification. Ethylenediamine (en), 1,3-propanediamine (pn), and 1,4,8,11-tetraazacyclotetradecane were obtained from Aldrich Chemicals. The ligand 1,5,8,12-tetraazadodecane [1,2-bis((aminopropyl)amino)ethane] was obtained from Strem Chemicals. KReO$_4$, triphenylphosphine, sodium hexafluorophosphate, obtained from Aldrich, were utilized without further purification.

Measurements. Infrared spectra were recorded on Perkin-Elmer 983G and 599 IR spectrometers using KBr pellets or Nujol Mülls. ^{1}H NMR spectra in DMF were collected on a Varian Gemini-300 spectrometer using the residual proton signal from the solvent as a reference. Magnetic susceptibilities measurements in D$_2$O solutions were obtained by the Evans method[8] on the same apparatus. Elemental analyses were accomplished on a Carlo Erba elemental analyzer, Model 1106. Analyses of impure microcrystalline samples were obtained using a Philips SEM 515 model scanning electron microscope equipped with EDAX Model Data Station. Metal ratios were conveniently determined by the integral counting of back-scattered X-ray fluorescence radiation; details of the complete experimental procedures have been reported elsewhere.[9] Conductivity measurements were performed in water solutions using an Amel Model 134 conductivity meter at $T = 20.5$ °C. Mass spectra were recorded on a VG 7070E mass spectrometer with ionization effected by electron impact.

Syntheses. Literature procedures were used to prepare the complexes ReNCl$_2$(PPh$_3$)$_2$ (**1**),[10a] ReCl$_4$(PPh$_3$)$_2$ (**2**),[10b,c] and ReCl$_3$(CH$_3$CN)(PPh$_3$)$_2$ (**3**).[10b–d] In the synthetic procedures described below, we noted that the presence of trace amounts of water are required for any reaction to proceed. When the syntheses were attempted in strictly anhydrous conditions, no reaction was observed.

***trans*-[ReO$_2$(L^1)]X [L^1 = H$_2$N(CH$_2$)$_3$NH(CH$_2$)$_2$NH(CH$_2$)$_3$NH$_2$; X = Cl, PF$_6$].** A 0.65-mmol quantity of the starting complex (**1**–**3**) was added

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Table I. Crystallographic Data

mol formula	$ReC_{10}H_{24}F_6N_4O_2P$	V, Å^3	853.2 (4)
fw	563.5	Z	2
space group	$P\bar{1}$, triclinic	ρ_{calcd}, g cm^{-1}	2.19
a, Å	5.533 (1)	μ, cm^{-1}	73.8
b, Å	11.899 (3)	transm coeff	0.48–1.0
c, Å	13.622 (3)	T, °C	21 ± 1
α, deg	89.78 (2)	R	0.063
β, deg	78.33 (2)	R_w	0.081
γ, deg	76.51 (2)		

to 40 mL of CH_2Cl_2 ($CHCl_3$) at room temperature. To the stirred mixture was added dropwise 0.56 g (3.2 mmol) of L^1 dissolved in 10 mL of EtOH within 5 min. The stirring was continued for 30 min at room temperature. A pale-yellow solid was collected by filtration, washed with cold CH_2Cl_2 ($CHCl_3$), acetone, and diethyl ether, and dried over P_2O_5 in vacuo. The yield was 58%. Conversion to the hexafluorophosphate salt was accomplished by addition of excess $NaPF_6$ (88 mg, 0.52 mmol) to a water solution (15 mL) of *trans*-$[ReO_2(L^1)]Cl$ (150 mg, 0.35 mmol). The solution was left to stand for 1 week to obtain the formation of yellow crystals, which were filtered out and washed with cold ethanol, diethyl ether, and hexane. Anal. Calcd for $C_8H_{22}N_4O_2RePF_6$: C, 17.89; H, 4.13; N, 10.42. Found: C, 17.96; H, 4.30; N, 10.26. IR (cm^{-1}): 790 (vs) (this band is also found in the IR spectrum of the corresponding Cl^- salt) [$\nu(ReO_2)$], 845 (s), 560 (s) [$\nu(PF_6)$]. MS (EI): m/z 393, 391 ($C_8H_{22}N_4ReO_2^+$). Λ_M (H_2O): 135 Ω^{-1} cm^2 mol^{-1} (Cl^- salt).

The complexes *trans*-$[ReO_2(L^2)_2]^+$ (L^2 = en, pn) were prepared using the same procedure detailed above, and their identity was confirmed by elemental analyses and mass spectra and by comparison of their infrared spectra with those reported in the literature for the same compounds prepared through a different route.[7,11]

***trans*-[ReO$_2$(cyclam)]X (cyclam = 1,4,8,11-Tetraazacyclotetradecane; X = ReO$_4$, Cl, PF$_6$).** To a stirred solution of the starting complex (**1**–**3**) (0.54 mmol) in CH_2Cl_2/EtOH ($CHCl_3$/EtOH) (40 mL, 3:1) was added a 3-fold excess of cyclam (324 mg, 1.6 mmol) as a solid, at room temperature. The solution became immediately turbid, producing a red-brown suspension. After 1 h of stirring the suspended solid faded away, and the solution became brown. This color became slowly clear, and after 4 h turned to faint yellow. After filtration, the volume of the solution was decreased to one-sixth by evaporation under reduced pressure. Addition of acetone led to the precipitation of a white-yellow solid, which was recrystallized from H_2O/EtOH to give a bright yellow microcrystalline powder of $[ReO_2(cyclam)](ReO_4)$ [**4**(ReO_4)] (yield 40%). Conversion to the chloride salt [**4**(Cl)] was accomplished as follows. A 250-mg quantity of **4**(ReO_4) (0.37 mmol) was dissolved in 30 mL of distilled water. $[As(C_6H_5)_4]Cl$ (234 mg, 0.56 mmol) was added to the solution, causing the immediate precipitation of white $[As(C_6H_5)_4][ReO_4]$ {IR: 912 cm^{-1} [$\nu(ReO_4)$], 1000 cm^{-1} [$\nu(As(C_6H_5)_4)$]}, which was filtered out by gravity. The residual solution was taken to dryness under reduced pressure, giving a pale-yellow solid, which was further redissolved in 10 mL of water. Acetone was added to the resulting solution, and a white-cream solid immediately precipitated. The mixture was allowed to stand for 10 min to ensure complete precipitation. The solid was collected on a medium-porosity frit, washed with EtOH, acetone, and diethyl ether, and aspirated to dryness. Metathesis to the hexafluorophosphate salt was accomplished as follows. A 250-mg quantity of **4**(ReO_4) (0.37 mmol) was dissolved in 30 mL of distilled water. $NaPF_6$ (94 mg, 0.56 mmol) was then added, and the resulting solution was left to stand for 20 days in a test tube. The crystals were successively washed with 3 × 5 mL of distilled water, 2 × 10 mL of cold ethanol, diethyl ether, and hexane and were collected by filtration. Anal. Calcd for $C_{10}H_{24}N_4O_2RePF_6$: C, 21.32; H, 4.29; N, 9.94. Found: C, 21.38; H, 4.42; N, 9.88. IR (cm^{-1}): 776 (vs), 809 (vs) [$\nu(ReO_2)$], 850, 560 [$\nu(PF_6)$] {772 cm^{-1} (vs) [$\nu(ReO_2)$] in both the ReO_4^- and Cl^- salts}. ^1H NMR (DMF) (ppm): 3.00 (dd, 8 H), 2.66 (t, 8 H), 2.04 (q, 4 H). MS (EI): m/z 419, 417 ($C_{10}H_{24}N_4ReO_2^+$), 403, 401 ($C_{10}H_{24}N_4ReO_2 - O^+$). Λ_M (H_2O): 95 Ω^{-1} cm^2 mol^{-1} (Cl^- salt).

When the reaction of the preparation of **4**(ReO_4) was stopped 5 min after the mixing of the reagents, a brilliant red-violet microcrystalline solid was collected by filtration. We failed to purify this intermediate product because of its conversion in solution to the compound **4**(ReO_4). A single microcrystal of the compound was analyzed by scanning electron microscopy (SEM) together with scanning electron microprobe analysis.[9] This technique gave a Re:Cl ratio 1:1 for the pure compound. IR (cm^{-1}): 910 (vs), 850 (m). MS (EI): m/z 419, 417 (M^+).

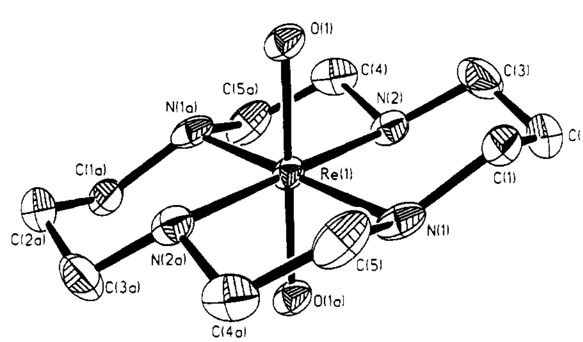

Figure 1. ORTEP (Johnson, C. K. ORTEP. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1980) diagram of cation **4**. Thermal ellipsoids are drawn at the 50% probability level.

Table II. Positional Parameters and Thermal Parameters for **4**(PF_6) with Estimated Standard Deviations in Parentheses

atom	x	y	z	U(eq), Å^2
Re(1)	0.0	0.0	0.0	0.020
O(1)	0.187 (2)	0.0543	0.0716 (8)	0.027
N(1)	−0.329 (2)	0.087 (1)	0.1003 (8)	0.027
N(2)	0.064 (2)	−0.1585 (8)	0.0776 (8)	0.025
C(1)	−0.329 (2)	0.063 (1)	0.209 (1)	0.033
C(2)	−0.276 (3)	−0.066 (1)	0.227 (1)	0.038
C(3)	−0.007 (3)	−0.136 (1)	0.188 (1)	0.043
C(4)	0.326 (2)	−0.224 (1)	0.035 (1)	0.037
C(5)	−0.383 (2)	0.218 (1)	0.076 (1)	0.034
Re(2)	0.5	0.5	0.5	0.019
O(2)	0.813 (1)	0.4457 (9)	0.4304 (8)	0.027
N(3)	0.361 (2)	0.409 (1)	0.398 (1)	0.032
N(4)	0.481 (2)	0.6568 (9)	0.4233 (9)	0.030
C(6)	0.443 (2)	0.434 (1)	0.2910 (9)	0.031
C(7)	0.388 (2)	0.565 (1)	0.275 (1)	0.035
C(8)	0.544 (3)	0.638 (1)	0.314 (1)	0.041
C(9)	0.641 (2)	0.722 (1)	0.466 (1)	0.030
C(10)	0.411 (2)	0.286 (1)	0.422 (1)	0.036

Table III. Selected Interatomic Distances (Å) for **4**(PF_6) with Estimated Standard Deviations in Parentheses

Re(1)–O(1)	1.78 (1)	Re(2)–O(2)	1.77 (1)
Re(1)–N(1)	2.09 (1)	Re(2)–N(3)	2.12 (2)
Re(1)–N(2)	2.15 (1)	Re(2)–N(4)	2.13 (1)

Table IV. Selected Bond Angles (deg) for **4**(PF_6) with Estimated Standard Deviations in Parentheses

O(1)–Re(1)–N(1)	89.6 (4)	O(2)–Re(2)–N(3)	89.6 (4)
O(1)–Re(1)–N(2)	89.1 (4)	O(2)–Re(2)–N(4)	89.6 (4)
N(1)–Re(1)–N(2)	97.1 (4)	N(3)–Re(2)–N(4)	97.9 (5)
Re(1)–N(1)–C(1)	114.5 (7)	Re(2)–N(3)–C(6)	114.0 (9)
Re(1)–N(1)–C(5)	108.1 (7)	Re(2)–N(3)–C(10)	108.7 (9)
Re(1)–N(2)–C(3)	111.2 (8)	Re(2)–N(4)–C(8)	112.7 (8)
Re(1)–N(2)–C(4)	107.4 (8)	Re(2)–N(4)–C(9)	106.7 (8)

Crystallographic Data Collection and Refinement of the Structure

A summary of data collection parameters is given in Table I. Data were collected on a yellow-orange needle-shaped crystal (0.08 × 0.08 × 0.20 mm^3) up to 2θ = 60° with a Nicolet-Siemens R3m/V four-circle automated diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). An empirical absorption correction, based on six reflections at χ = 90° for different azimuthal angles (ψ-scan) was made. As is frequently the case,[12] the anion associated with similar structures is less than well-behaved; the counteranions are disordered, and six additional fluorine atoms were used to attempt to compensate for this; the original and additional fluorine atoms were given variable site occupancies, with the constraint that the sum of fractional occupancies for each disordered atom was one, by using a common fixed isotropic thermal parameter. The procedure was unsuccessful, and we decided to maintain

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the 12 fluorine atoms in the positions found in the final difference map with occupancies equal to 0.5. At this stage, the refinement was concluded, since any further attempt (for example, the treatment of PF$_6^-$ as a rigid body) gave a physically less meaningful model. Nevertheless, the largest peaks on the final difference map were near the PF$_6^-$ ions along with two peaks, up to 2.6 and 2.4 e Å^{-3}, at 0.73 and 0.74 Å far from Re(1) and Re(2), respectively. The averaged distance and angle in PF$_6^-$ are 1.58 Å and 86° (F–P–F), respectively. The programs used are part of the Siemens SHELXTL-PLUS (release 4.1) system.[13] Full-matrix least-squares refinement minimized $\Sigma w(|F_o| - |F_c|)^2$, $w^{-1} = \sigma^2(F) + 0.0029F^2$, using 3006 observed reflections [$F_o > 3\sigma(F_o)$]. An ORTEP view of the cation is shown in Figure 1. Selected positional parameters and bond distances and angles are found in Tables II–IV.

Results and Discussion

Synthesis. The reactions of bidentate [$H_2N(CH_2)_nNH_2 = L^2$, n = 2, 3] and tetradentate [$H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2 = L^1$] chelating amines with the complexes Re^{V}NCl$_2$(PPh$_3$)$_2$ (**1**), Re^{IV}Cl$_4$(PPh$_3$)$_2$ (**2**), and Re^{III}Cl$_3$(CH$_3$CN)(PPh$_3$)$_2$ (**3**), at room temperature, in CHCl$_3$ or CH$_2$Cl$_2$/EtOH mixtures, invariably led to the precipitation of the monocationic complexes *trans*-[ReO$_2$(L^n)$_n$]Cl (n = 1, 2) in good yields. The same reactions carried out using the macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane (cyclam) gave rise to the dioxo complex *trans*-[ReO$_2$(cyclam)](ReO$_4$) [**4**(ReO$_4$)] in which perrhenate was present as the counterion. The formation of perrhenate was not observed with the ligands L^1 and L^2. The reactions of cyclam with complexes **1**–**3** occur through the formation of an intermediate complex which was precipitated as a red-violet microcrystalline solid a few minutes after the mixing of the reagents. We were unable to fully characterize this solid owing to the presence of metal-containing impurities that were difficult to remove by chromatography. Moreover, we found that this intermediate product transformed slowly in aqueous solution into the complex **4**(ReO$_4$). Mass spectral data and electron microprobe analysis of microcrystals of the compound are consistent with the formulation [ReO$_2$(cyclam)]Cl. A possible tentative assignment of its structure is that of the isomeric form *cis*-[ReO$_2$(cyclam)]$^+$. In a previously reported characterization this compound was formulated as the tricationic complex [ReO(cyclam)(OH$_2$)]Cl$_3$.[14]

The hexachloro complex [ReCl$_6$]$^{2-}$ has been considered as the common starting material for the syntheses of coordination compounds containing the [ReO$_2$]$^+$ unit. In particular, *trans*-dioxorhenium(V) complexes with chelating amines and pyridine ligands have been obtained from K$_2$ReCl$_6$ in the presence of air and under very forcing conditions.[15] These reactions are slow, and this fact was interpreted as due to the preliminary oxidation of Re^{4+} to Re^{5+} by dioxygen in order to produce the [Re^{V}O$_2$]$^+$ moiety.[7] Very recently, the complexes Re^{V}OCl$_3$(PPh$_3$)$_2$ and *cis*-Re^{V}O$_2$I(PPh$_3$)$_2$ have been used as suitable starting materials for the synthesis of amine, pyridine, and cyclam complexes containing the [ReO$_2$]$^+$ unit.[6,7,16] Reactions proceed quickly and give high yields of products under mild conditions. At first sight, this enhanced reactivity might be ascribed to the presence of the Re^{5+} center and oxo ligands on the starting complexes. However, the results presented here contradict this view. They indicate that the formation of the [ReO$_2$]$^+$ group takes place easily also when acyclic and cyclic chelating amines react with the complexes **1**–**3** which contain the rhenium atom in different oxidation states and do not carry O^{2-} groups. It appears, therefore, that the reactions of mixed halogen–phosphine complexes of rhenium with ligands having neutral nitrogen donor atoms provide a general and convenient route to the synthesis of cationic complexes containing the [ReO$_2$]$^+$ group. This result is particularly emphasized by the substitution of the stable [Re≡N]$^{2+}$ core by the *trans*-[ReO$_2$]$^+$ group in the reactions involving the rhenium(V) nitrido complex **1**. At present, no examples of cleavage of the Re≡N bond are known, this group being also resistant to strong oxidizing agents like hydrogen peroxide. The easy removal of the N^{3-} group described here is remarkable, particularly when compared with the behavior of the analogous technetium(V) nitrido complex TcNCl$_2$(PPh$_3$)$_2$, which gives rise to the cationic complexes [TcN(L^n)$_n$Cl]$^+$ (n = 1, 2) and [TcN(L)Cl]$^+$ in reacting with the amine ligands L^{1,2} and tetraazamacrocycles (L), without loss of the [Tc≡N]$^{2+}$ group.[2,3] The oxidation state of the rhenium atom seems to play a minor role in the formation of the [ReO$_2$]$^+$ group, as shown by the reactions of compounds **2** and **3** which require the oxidation of the Re^{4+} and Re^{3+} ions to produce the final Re^{5+} complexes.

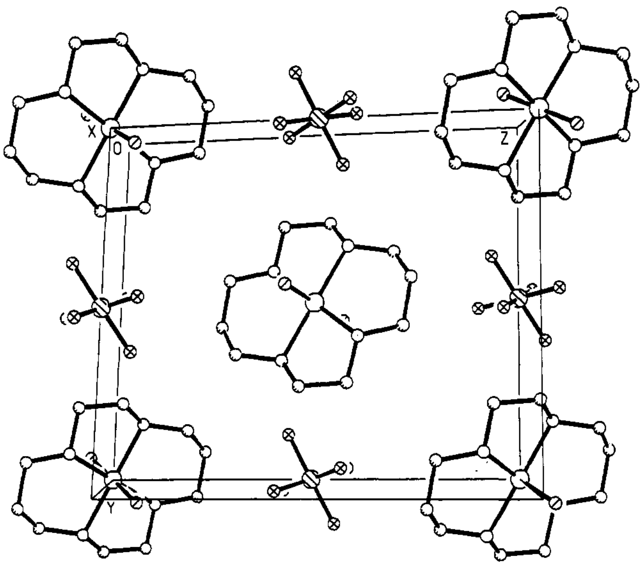

Figure 2. Crystal packing diagram (ORTEP).

Crystal Structure of *trans*-[ReO$_2$(cyclam)](PF$_6$). The structure of the monomeric octahedral complex **4**(PF$_6$) is shown in Figure 1, and the content of the unit cell is reported in Figure 2 as a representative projection. The crystal structure consists of two independent cations [Re atoms at (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$)] and anions [P atoms at (0, $^1/_2$, 0) and (0, 0, $^1/_2$)], and each ion has a crystallographically imposed center of symmetry. The cations/anions are well-separated, the shortest nonbonding approach (3.06 Å) occurring between a fluorine atom and C(4) (at $-1 + x$, y, z). The macrocyclic ligand shows the expected *RRSS* (*trans*-III) conformation.[17] The structure of the present complex exhibits close geometrical resemblances with the structures of the *trans*-dioxo complexes [ReO$_2$(cyclam)Cl·2[B(C$_6$H$_5$)$_3$·H$_2$O] [**4**-(BPh$_3$)][16] and [TcO$_2$(cyclam)]ClO$_4$·H$_2$O,[18] reported previously. The weighted rms deviation, dervied from the BMFIT program,[19] is 0.04 Å, confirming that the three structures are nearly superimposable. Bond lengths and angles do not differ significantly from the expected values, and they will not be discussed further here. Interatomic contacts in the molecular packing have been observed only between O(1) and N(1) atoms (at $1 - x$, $1 - y$, $1 - z$) and O(2) and N(3) atoms (at $1 - x$, $1 - y$, $1 - z$) (2.89 and 2.90 Å, respectively) having the appropriate geometrical orientation for the setting of a possible weak hydrogen bonding [O(1)···H–N(1) 161.1° and O(2)···H–N(3) 162.2°].

Infrared Spectra. The complex *trans*-[ReO$_2$(L^1)]$^+$ exhibits a single absorption at 790 cm^{-1} in the IR spectrum assigned to the asymmetric stretching vibration of the *trans*-[ReO$_2$]$^+$ group. This

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result does not parallel a previous observation on similar rhenium(V) dioxo complexes with acyclic tetraamines exhibiting *two* IR bands at 810 and 790 cm^{-1} attributed to the stretching vibrations of the same group.[6] The complex cation *trans*-$[ReO_2(cyclam)]^+$ (**4**) shows both types of absorptions assigned to the *trans*-$[ReO_2]^+$ group depending on the particular counterion in the salts **4**(ReO_4), **4**(Cl), and **4**(PF_6). The complexes **4**(ReO_4) and **4**(Cl) have *one* band at 772 cm^{-1}, and **4**(PF_6) has *two* bands at 809 and 776 cm^{-1}. Previously, it has been reported that the salt $[ReO_2(cyclam)Cl{\cdot}2[B(C_6H_5)_3{\cdot}H_2O]$ [**4**(BPh_3)] exhibits *one* absorption at 825 cm^{-1}.[16] The presence of a *single* or *double* absorption in complexes containing the *trans*-MO_2 arrangement is not uncommon, and a similar behavior has been observed for *trans*-OsO_2^{2+} and *trans*-UO_2^{2+} complexes.[20] This behavior has been generically attributed to unit-cell coupling.[6,21] However, the X-ray crystallographic analysis of **4**(PF_6) shows that the complex cation $[ReO_2(cyclam)]^+$ lies on an inversion center (Figure 2). Since the site group does not alter the inversion symmetry of the free cation, it seems unlikely that the doubling of the $[ReO_2]^+$ stretch in **4**(PF_6) originates from unit-cell splitting. Considering that the unit cell of **4**(PF_6) includes two molecules of the complex cation which are not related by any symmetry operation of the space group, we suggest assignment of the two observed absorptions to the *single* asymmetric stretching of the $[ReO_2]^+$ group associated with each one of the two inequivalent sets of molecules. This interpretation is consistent with the finding that the unit cell of **4**(BPh_3), which shows *one* IR absorption, includes two symmetry-equivalent molecules of cation **4**.[16] The observed differences in the values of the *trans*-dioxo asymmetric stretching frequencies between the species **4**(Cl), **4**(BPh_3), and the two independent complex cations in **4**(PF_6) may be probably ascribed to van der Waals interactions of the different crystalline environments. Similar effects have been already observed, and Bandoli et al. reported a definite example of the change of the IR stretching frequencies upon variation of the crystalline form for the technetium(III) complex $Tc(pd)_2(PPh_3)Cl$ (pd = pentane-2,4-dionato).[22]

Acknowledgment. S.A.L. is grateful to the Italian Ministero degli Esteri for a grant at the University of Ferrara. We thank M. Fratta for elemental analyses, L. Zuppiroli for mass spectral measurements, and A. Aguiari for scanning electron microprobe analysis. This work was supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica.

Registry No. **1**, 25685-08-9; **2**, 16853-54-6; **3**, 34387-57-0; **4**(ReO_4), 141040-25-7; **4**(Cl),, 117579-37-0; **4**(PF_6), 141040-26-8; *trans*-$[ReO_2(L')]Cl$, 140874-56-2; *trans*-$[ReO_2(L')]PF_6$, 140874-58-4; *trans*-$[ReO_2(en)_2]Cl$, 14405-69-7; *trans*-$[ReO_2(pn)_2]Cl$, 93192-00-8.

Supplementary Material Available: Tables of all refined atomic coordinates (Table A), anisotropic thermal parameters (Table B), and complete bond distances and angles (Table C) and ORTEP diagrams of the conformation of the cyclam ligand (Figure 3) and of the possible network of intermolecular hydrogen bondings (Figure 4) in $[ReO_2(cyclam)](PF_6)$ (6 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Low-Dimensional Molecular Metals $(Per)_2M(mnt)_2$ (M = Fe and Co)

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Received July 13, 1991

Single crystals of the quasi-one-dimensional conductors $(Per)_2M(mnt)_2$, M = Fe and Co (Per = perylene, mnt = maleonitriledithiolate), were prepared by electrocrystallization. By X-ray diffraction at room temperature and with synchrotron radiation (λ = 0.89 Å, at Daresbury), the $(Per)_2Fe(mnt)_2$ compound was shown to crystallize in the monoclinic space group $C2/c$ with cell parameters a = 50.571 (6) Å, b = 8.212 (2) Å, c = 17.726 (9) Å, β = 92.43 (1)°, and Z = 8. An average crystal structure was obtained at 295 K using a conventional X-ray source, on the basis of the monoclinic space group $P2_1/n$ with a = 17.665 (3) Å, b = 4.098 (2) Å, c = 25.219 (3) Å, β = 92.43 (2)°, and Z = 2. The average crystal structure of $(Per)_2Fe(mnt)_2$ at room temperature consists of a close-packed arrangement of segregated stacks of perylene and $Fe(mnt)_2$ units. ^{57}Fe Mössbauer spectroscopy shows the dimerization of the $Fe(mnt)_2$ units with the Fe atom in a square pyramidal coordination by sulfur atoms without significant changes within the temperature range 15–295 K. For both compounds, room temperature values of electrical conductivity and absolute thermoelectric power are $\sigma_{RT} \simeq 200\ \Omega^{-1}\ cm^{-1}$ and $S_{RT} = 42\ \mu V/K$, respectively. They exhibit metallic behavior down to 58 and 73 K, for M = Fe and Co, respectively, where a metal–insulator transition occurs. The paramagnetic susceptibility of the Co compound is due to a Pauli-like contribution of the perylene chains of 3.2×10^{-4} emu mol^{-1} at 300 K that vanishes at the metal–insulator transition, while that of the Fe compound is dominated by the contribution of antiferromagnetically coupled pairs of $S = {}^3/_2$ spins in the $[Fe(mnt)_2]_2^{2-}$ units, in a way similar to the magnetic susceptibility of $[(C_2H_5)_4N]_2[Fe(mnt)_2]_2$ and $[(n\text{-}C_4H_9)_4N]_2[Fe(mnt)_2]_2$. These properties and the average crystal structure are compared with the correspondent ones for other metallic members of the $Per_2M(mnt)_2$ family.

Introduction

Several molecular metals based on perylene (Per (I)) and on square planar anionic metal complexes ($M(mnt)_2$ (II), where mnt = maleonitriledithiolate or *cis*-2,3-dimercapto-2-butenedinitrile) with the general formula $(Per)_2M(mnt)_2$, where M = Pt, Pd, Au, Cu, and Ni, have been studied in the last years.[1-6]

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