Notes

A Spectroscopic and Crystallographic Study of the $[ReNCl_4]^-$ Ion

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Preparation of $[AsPh_4][ReNCl_4]$ was accomplished by the addition of $ReNCl_4$ to $[AsPh_4]Cl$ in $POCl_3$. The crystal structure and the i.r. spectra reveal the nearly ideal C_{4v} symmetry of the $[ReNCl_4]^-$ ion. The force constant of the Re≡N bond is in agreement with the observed Re≡N length of 1.619(10) Å. The Re–Cl bond distance, 2.322(2) Å, is the first to be reported for a Re^{VI} case. Unit-cell parameters are in close agreement with those of the other members of the isostructural series: a = 12.776(4), c = 7.778(3) Å, Z = 2, and D_c = 1.90 g cm^{-3} in the tetragonal space group $P4/n$. Least-squares refinement gave a final R value of 0.022 for 534 unique observed reflections.

COMPLEXES of the $[MNCl_4]^-$ ion are well known for the transition metals molybdenum, tungsten, ruthenium, and osmium.[1-5] Some of their tetraphenylarsonium derivatives have been characterized by X-ray crystallographic determinations. The complexes contain metal–nitrogen triple bonds (symmetry C_{4v}), as shown by the short metal–nitrogen bond lengths [Mo≡N, 1.66(1) Å;[2] Ru≡N, 1.57(1) Å;[4] and Os≡N, 1.60(1) Å [5]]. The π portion of the triple bond is formed by the overlap of the empty degenerate d_{xy}, d_{xz} orbitals with the filled p_x, p_y orbitals of the terminal nitrogen ligand. In the i.r. spectrum the metal–nitrogen group gives a strong characteristic stretching frequency in the region 1 000—1 100 cm^{-1}.[1-3] The caesium and tetraphenylarsonium salts of the $[ReNCl_4]^-$ ion are mentioned in the literature [3] and $[AsPh_4][ReNCl_4]$ [6] was recently used as starting material to prepare $[AsPh_4]_2[ReN(NCS)_5]$.[7] An e.s.r. study of the $[ReNCl_4]^-$ ion doped into the $[AsPh_4][RuNCl_4]$ host has also appeared.[8]

In connection with our studies in the field of transition-metal nitrogen chemistry we recently prepared the first example of a new class of rhenium–nitrogen compound, $ReNCl_4$,[9] which contains rhenium in the 7+ oxidation state. This compound is an excellent starting material to prepare many complexes containing rhenium–nitrogen triple bonds. Herein we report the crystal structure and i.r. spectroscopy of $[AsPh_4][ReNCl_4]$, which was obtained from the reaction of $ReNCl_4$ with $[AsPh_4]Cl$ in $POCl_3$.

EXPERIMENTAL

Preparations.—All manipulations were conducted *in an* atmosphere of nitrogen. Solvents and starting materials were carefully dried prior to use.

Infrared Spectra.—Spectra were recorded on a Perkin-Elmer 577 spectrophotometer. The complexes were sampled as Nujol suspensions between CsBr plates.

Preparation of $[NMe_4][ReNCl_4]$.—The compound $ReNCl_4$ (0.694 g), prepared by the reaction of $ReCl_5$ with excess of nitrogen trichloride, was mixed with tetramethylammonium chloride (0.222 g, Merck). During the time the mixture was stirred, $POCl_3$ (10 cm^3) was added dropwise. After 3 d the reaction was complete. The red suspension was filtered off an insoluble product, and $POCl_3$ (5 cm^3) was distilled under vacuum. Cooling the solution to 5 °C yielded yellow crystals (0.550 g). They were washed with a small amount of methylene chloride and dried under vacuum (Found: C, 11.55; H, 2.80; Cl, 34.25; N, 6.80; Re, 45.3. Calc. for $C_4H_{12}Cl_4N_2Re$: C, 11.55; H, 2.90; Cl, 34.1; N, 6.75; Re, 44.75%).

Preparation of $[AsPh_4][ReNCl_4]$.—The compound $ReNCl_4$ (0.619 g) was mixed with $[AsPh_4]Cl$ (0.758 g, Fluka) and $POCl_3$ (10 cm^3) as described above. After 2 d a yellow microcrystalline powder (0.500 g) was filtered off. The compound was redissolved and the solution cooled to 5 °C for several days. The resulting yellow crystals were washed with methylene chloride and dried under vacuum. Both samples have the same composition (Found: C, 39.55; H, 2.65; Cl, 19.3; N, 1.95; Re, 25.4. Calc. for $C_{24}H_{20}AsCl_4NRe$: C, 39.7; H, 2.75; Cl, 19.55; N, 1.95; Re, 25.7%).

X-*Ray Data Collection, Structure Determination, and Refinement for* $[AsPh_4][ReNCl_4]$.—*Crystal data.* $C_{24}H_{20}AsCl_4NRe$, M 725.4, Tetragonal, a = 12.776(4), c = 7.778(3) Å, U = 1 269.6 Å^3, Z = 2, D_c = 1.90 g cm^{-3}, $F(000)$ = 694, μ(Mo-K_α) = 68.7 cm^{-1}, λ = 0.710 7 Å, space group $P4/n$. The lattice parameters were determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 30°$) accurately centred on an Enraf–Nonius CAD-4 diffractometer.

A crystal of dimensions 0.45 × 0.55 × 0.30 mm was sealed in a thin-walled capillary under a nitrogen atmosphere. Data were collected on the diffractometer with graphite-crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω—2θ scan technique in a manner similar to that previously described.[10] All reflections in one independent octant out to $2\theta \leqslant 50°$ were measured; 534 were considered observed [$I \geqslant 3\sigma(I)$].

TABLE 1

Final fractional co-ordinates for $[AsPh_4][ReNCl_4]$ with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Re	0.000 00	0.500 00	0.381 47(8)
As	0.000 0	0.000 0	0.500 0
Cl	0.091 0(2)	0.651 5(2)	0.311 8(3)
N	0.000 0	0.500 0	0.589 6(13)
C(1)	−0.117 9(5)	0.012 8(6)	0.350 9(8)
C(2)	−0.193 4(6)	0.088 8(6)	0.382 5(10)
C(3)	−0.274 4(6)	0.099 8(7)	0.265 1(12)
C(4)	−0.279 8(7)	0.035 4(8)	0.124 0(11)
C(5)	−0.207 0(7)	−0.040 5(7)	0.096 7(11)
C(6)	−0.124 8(6)	−0.053 5(6)	0.211 2(9)
H(1)[C(2)]	−0.191 4	0.134 9	0.482 0
H(2)[C(3)]	−0.327 1	0.155 5	0.278 5
H(3)[C(4)]	−0.340 8	0.041 2	0.039 4
H(4)[C(5)]	−0.212 1	−0.087 1	−0.008 7
H(5)[C(6)]	−0.074 3	−0.108 3	0.192 3

The intensities were corrected for Lorentz, polarization, and absorption effects.

Full-matrix least-squares refinement was carried out using the Busing and Levy ORFLS program.* The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for Re, As, Cl, N, and C were taken from Cromer and Waber,[11] and the scattering for rhenium and arsenic was corrected for the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.[12] Scattering factors for hydrogen were from ref. 13.

The position of the rhenium atom was deduced from the inspection of a Patterson map and the subsequent calculation of Fourier-difference maps allowed the location of the remaining non-hydrogen atoms. Refinement with isotropic temperature factors led to a reliability index of $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.092$. Conversion to anisotropic thermal parameters and further refinement gave $R_1 = 0.035$. The hydrogen atoms of the phenyl group were placed at calculated positions 1.00 Å from the bonded carbon atoms and their parameters were not refined. Additional cycles of refinement led to final R values of $R_1 = 0.022$ and $R_2 = [\Sigma(|F_o| - |F_c|)^2/\Sigma(F_o)^2]^{\frac{1}{2}} = 0.025$. The largest parameters shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. A final difference Fourier showed no feature greater than 0.4 e Å^{-3}. The standard deviation of an observation of unit weight was 0.85. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ *vs.* $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table 1. The observed and calculated structure factor amplitudes are given in Supplementary Publication No. SUP 22988 (7 pp.).†

TABLE 2

Comparison of metal–nitrogen stretching modes, force constants, and bond lengths of $[MNCl_4]^-$ complexes with C_{4v} symmetry

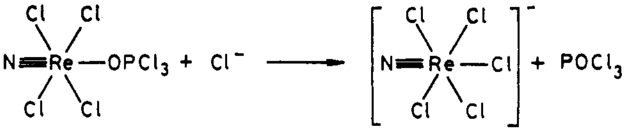
Compound	$r(M\equiv N)$/Å	$\nu(MN)$/cm^{-1}	$f(MN)$/mdyn Å^{-1} [a]
$[As(C_6H_5)_4][MoNCl_4]$	1.66 [2]	1 054 [1]	8.1
$[As(C_6H_5)_4][WNCl_4]$	(1.65) [b]	1 036 [1]	8.1
$[As(C_6H_5)_4][ReNCl_4]$	1.619(10) [c]	1 085 [c]	9.0
$[As(C_6H_5)_4][RuNCl_4]$	1.57 [4]	1 092 [d]	8.6
$[As(C_6H_5)_4][OsNCl_4]$	1.60 [5]	1 123 [d]	9.6

[a] Throughout this paper 1 dyn = 10^{-5} N. [b] Calculated value [c] This work. Estimated standard deviation is given in parentheses. [d] W. P. Griffith and D. Pawson, *J. Chem. Soc., Dalton Trans.*, 1973, 1315.

RESULTS AND DISCUSSION

The $[ReNCl_4]^-$ complex was prepared by the interaction of both tetramethylammonium chloride and tetraphenylarsonium chloride, respectively, with equimolar amounts of $ReNCl_4$ in the presence of $POCl_3$.

For the reaction mechanism it can be assumed that the $POCl_3$ molecule, which forms a 1 : 1 unstable complex with $ReNCl_4$ [9] and serves as solvent, is displaced by a chloride ligand in the first step [equation (1)]. Subsequently, the Cl ligand in the less favoured *trans* position to the nitrido-ligand is split off and the rhenium is reduced simultaneously from Re^{VII} to Re^{VI}, forming the $[ReNCl_4]^-$ ion [overall, equation (2)].



(1)

$$ReNCl_4 + Cl^- \longrightarrow [ReNCl_4]^- + \tfrac{1}{2}Cl_2 \quad (2)$$

I.r. Spectra.—The crystal structure shows the nearly ideal C_{4v} symmetry of the $[ReNCl_4]^-$ ion. The i.r. spectra of both the NMe_4^+ and the $AsPh_4^+$ complex agree with this result. The ReN stretching mode (A_1) can be assigned to the absorptions at 1 089 and 1 085 cm^{-1}, respectively. This is well established in other complexes containing transition-metal–nitrogen triple bonds (see Table 2). The force constant of the Re≡N bond also is in good agreement with the Re≡N bond length of 1.619(10) Å and allows the prediction of the length of the W≡N bond in the corresponding $[WNCl_4]^-$ complex, for which the crystal structure determination has not yet been carried out (Table 2). For the calculations of the metal–nitrogen force constants the simple two-mass formula was used. This is acceptable because of the relatively large metal : nitrogen mass ratio, while the coupling with the deformation modes of the $ReCl_4$ group is small and is of the same order of magnitude as the other complexes containing C_{4v} symmetry listed in Table 2. In the region of the rhenium chloride-stretching modes we observed a strong absorption at 341 and 346 cm^{-1} for $[NMe_4][ReNCl_4]$ and $[AsPh_4][ReNCl_4]$, respectively, which can be assigned to the E mode, whereas a shoulder at 358 cm^{-1} is due to the symmetric stretching mode (A_1). The T_d symmetry of the NMe_4^+ cation is only slightly lowered,

TABLE 3

Bond lengths (Å) and angles (°) for $[AsPh_4][ReNCl_4]$

(*a*) Bond lengths

Re–N	1.619(10)	C(3)–C(4)	1.373(12)
Re–Cl	2.322(2)	C(4)–C(5)	1.361(12)
As–C(1)	1.908(6)	C(5)–C(6)	1.387(11)
C(1)–C(2)	1.390(10)	C(6)–C(1)	1.381(9)
C(2)–C(3)	1.387(10)		

(*b*) Bond angles

N–Re–Cl	103.49(6)	C(1)–C(2)–C(3)	118.2(7)
Cl–Re–Cl′ [a]	86.88(3)	C(2)–C(3)–C(4)	120.2(8)
Cl–Re–Cl″ [b]	153.01(12)	C(3)–C(4)–C(5)	121.1(8)
C(1)–As–C(1)′	105.1(4)	C(4)–C(5)–C(6)	120.2(8)
C(1)–As–C(1)″	111.7(2)	C(5)–C(6)–C(1)	118.7(7)
C(2)–C(1)–C(2)	121.6(7)		

[a] Primed atoms related to those in Table 1 by ($\frac{1}{2} - y, \frac{1}{2} + x, z$). [b] Related to those in Table 1 by ($-x, 1 - y, z$).

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* Other crystallographic programs used on a Univac 1110 include ORFFE (distances and angles with e.s.d.s, by W. R. Busing, K. O. Martin, and H. A. Levy), FOURIER (Fourier synthesis, D. J. Hodgson's version of Dellaca and Robinson's program), ORTEP (thermal ellipsoid drawings, by C. K. Johnson), and BPL (least-squares planes, by W. E. Hunter).

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

as shown by the splitting of the A_2 $\mathrm{NC_4}$ stretching mode in the strong absorption at 950 cm^{-1} and the shoulder at 925 cm^{-1}.

Crystal Structure.—The structure and atom-numbering scheme for the anion is shown in Figure 1, while that for the cation is given in Figure 2. The title compound is isostructural with the other members of the series $[\mathrm{AsPh_4}][\mathrm{MNCl_4}]$ (where M = Mo,[2] W,[1] Ru,[4] or Os [5]), and with $[\mathrm{AsPh_4}][\mathrm{MoOCl_4}]$.[2,14] The parameters of the $\mathrm{AsPh_4}^+$ ion (Table 3) are normal for this type of compound.

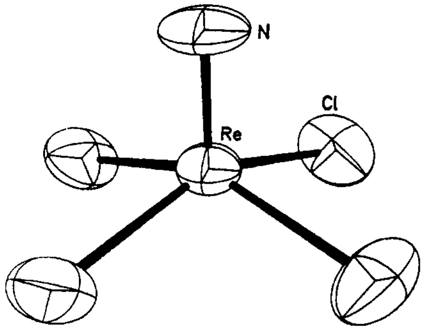

FIGURE 1 Structure of the $[\mathrm{ReNCl_4}]^-$ anion with the atoms represented as their 40% probability ellipsoids for thermal motion

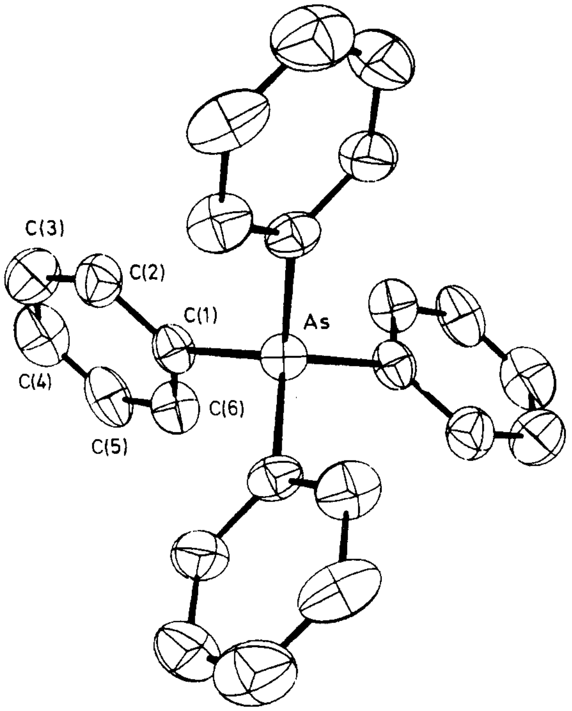

FIGURE 2 Structure of the $\mathrm{AsPh_4}^+$ cation showing the atom numbering

The Re≡N bond length of 1.619(10) Å is shorter than the 1.657(12) Å distance found in $[\mathrm{AsPh_4}][\mathrm{ReN(NCS)_5}]$,[7] the only other reported $\mathrm{Re^{VI}}$ structure. The length correlates well with the i.r. spectral interpretation as shown in Table 2. The Re–Cl bond distance, 2.322(2) Å, cannot be compared with any $\mathrm{Re^{VI}}$ case, but the $\mathrm{Re^{V}}$ complex $[\mathrm{ReNCl_2(PPh_3)_2}]$ [15] exhibits a Re–Cl separation of 2.377 Å. One would expect a contraction for $\mathrm{Re^{VI}}$ compared to $\mathrm{Re^{V}}$. The bond angles in the anion, N–Re–Cl = 103.49(6)° and Cl–Re–Cl′ = 86.88(3)°, are comparable to those in the isostructural series. In $[\mathrm{AsPh_4}][\mathrm{RuNCl_4}]$ [4] the corresponding values are 104.58(4) and 86.37(5)°.

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