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The Crystal and Molecular Structure of Tetraammineplatinum(II) μ-Oxo-bis[oxotetracyanorhenium(V)]

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The crystal structure of the μ-oxo-bis[oxotetracyanorhenium(V)] ion, $ORe(CN)_4ORe(CN)_4O^{4-}$, has been determined as the tetraammineplatinum(II) salt using scintillation counter techniques in a three-dimensional X-ray diffraction study. The compound crystallizes in the monoclinic space group $C2/m$ with unit cell dimensions $a = 14.778$ (2) Å, $b = 9.517$ (2) Å, $c = 11.267$ (2) Å, and $\beta = 130.21$ (2)°. The density of 3.167 (1) g/cm^3, calculated on the basis of two formula units per unit cell, agrees with the flotation density of 3.16 (1) g/cm^3. The structure was resolved by Patterson and Fourier methods and refined by full-matrix least-squares treatment to a conventional R factor of 3.2% using 1729 independent reflections whose intensities were above background. The two independent $Pt(NH_3)_4^{2+}$ ions are planar with an average Pt–N distance of 2.051 (9) Å. The anion is binuclear with a linear OReOReO grouping with the cyanide ligands completing an octahedron about each rhenium. The data are most consistent with the cyanide ions being carbon bonded with an average Re–C distance of 2.120 (7) Å. The bridging Re–O distance is 1.915 (1) Å and the terminal Re–O distance is 1.698 (7) Å.

Introduction

The aqueous chemistry of the 4+ to 8+ oxidation states of metal ions revolves around various types of hydrolysis reactions. In many cases -yl ions of the type MO^{n+}, MO_2^{n+}, and MO_4^{n-} are the predominant aqueous species. For the first two types other ligands (including water) complete the metal ion coordination sphere. A relatively small number of examples of nontetrahedral -yl complexes are known of which very few have the characteristic of slow ligand exchange for both types of ligands. Thermodynamic and kinetic studies on this type of complex can contribute significantly to our understanding of the nature of the bonding interaction. A complex ion well suited to a study of this type is $ReO_2(CN)_4^{3-}$, and such a study has recently been completed.[2] During that study a clean, previously unrecognized dimerization reaction was observed which led to the isolation of the anion $ORe(CN)_4ORe(CN)_4O^{4-}$. Oxygen-18 kinetic exchange data and other types of evidence suggested but did not prove this structure for the ion. A further interest lies in the two types of Re–O bonds present in the ion, both of which are no doubt stronger than single Re–O bonds. In order to establish the molecular structure, a single-crystal structure determination has been done. A comparison was needed with the so-called "double bonds" in *trans*-$ReO_2(CN)_4^{3-}$, and its structure was redetermined to obtain higher precision and has recently been reported.[3]

Thus, this paper reports the crystal structure of $[Pt(NH_3)_4]_2[Re_2O_3(CN)_8]$ and compares the anion structure with molecular structures of complexes such as *trans*-$ReO_2(CN)_4^{3-}$, $Br_4ReO(OH_2)^-$, $Re_2OCl_{10}^{4-}$, $Ru_2OCl_{10}^{4-}$, $Re_2O_3(S_2CN(C_2H_5)_2)_4$, and ReO_4^-.

Experimental Section

Crystal Preparation.—The method of Toppen and Murmann[2] was used to prepare $K_4Re_2O_3(CN)_8$. Numerous simple salts of $ORe(CN)_4ORe(CN)_4O^{4-}$ yielded unsatisfactory crystals for detailed X-ray study. The sparingly soluble $Pt(NH_3)_4^{2+}$ salt was obtained by the addition of a solution of $[Pt(NH_3)_4]Cl_2$ to one of $K_4[Re_2O_3(CN)_8]$. The final single crystals were obtained by cooling a saturated aqueous solution of the salt $[Pt(NH_3)_4]_2[Re_2O_3(CN)_8]$.

Data Collection.—Preliminary precession photographs of the violet crystals indicated a monoclinic cell. The systematic absences observed on the photographs were $h + k$ odd for hkl indicating the space group $C2/m$, Cm, or $C2$.

Because of the high absorption coefficient ($\mu = 227$ cm^{-1}) it was necessary to choose a small crystal for intensity measurements (approximately 0.03 mm × 0.04 mm × 0.09 mm). This crystal was bounded by 14 faces, all of small indices.

The crystal was centered on a Picker four-circle diffractometer with the crystal's b axis coincident with the ϕ axis of the diffractometer, and the setting angles of 30 intense reflections were determined using Mo Kα radiation (λ 0.7107 Å). The cell constants as determined by a least-squares refinement[4] using these 30 reflections were $a = 14.778$ (2) Å, $b = 9.517$ (2) Å, $c = 11.267$ (2) Å, and $\beta = 130.21$ (2)°. The density calculated for two formula units per unit cell was 3.167 (1) g/cm^3, which agrees well with the observed density of 3.163 (10) g/cm^3 obtained by flotation methods in a mixed-solvent system. The refinement using the 30 reflections was used to calculate the setting angles for all reflections measured. The intensities of 3313 reflections were measured out to a 2θ angle of 65°. The count rate never exceeded 8000 counts/sec and was thus in the linear region of the counter. The diffracted Mo Kα radiation was filtered through 1 mil of niobium foil in front of a 3 mm × 3 mm receiving aperture at a takeoff angle of 2.0°. A scan rate of 1.0°/min was used for the variable nonsymmetric 2θ scan. This scan was taken from 0.33° below the 2θ setting for Kα_1 (λ 0.70926 Å) to 0.38° above the 2θ setting for Kα_2 (λ 0.71354 Å). Stationary background counts of 20 sec were taken at both the high- and low-angle ends of the scan. Five reflections chosen as standards were measured every 4 hr as a check on crystal and instrument stability. No significant change in intensity of these reflections was observed.

Data Reduction.—Corrections for background and Lorentz–polarization effects and the counting statistics standard deviations were calculated using the formulas previously described.[5] The dimensions of the crystal and the indices of the faces were determined by optical goniometric and microscopic techniques. All reflection intensities were corrected for absorption. The absorption correction factor ranged from 0.29 to 0.61.

From the 3313 measured intensities, 2109 independent data points were obtained of which 1729 had intensities greater than

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[1] Taken in part from the Ph.D. Dissertation of R. Shandles, University of Missouri, 1971.

[2] D. L. Toppen and R. K. Murmann, *Inorg. Nucl. Chem. Lett.*, **6**, 139 (1970); D. L. Toppen, Ph.D. Dissertation, University of Missouri, Columbia, 1970.

[3] R. K. Murmann and E. O. Schlemper, *Inorg. Chem.*, **10**, 2352 (1971).

[4] All calculations were performed on the IBM 360/65 computer of the University of Missouri Computer Research Center using the following programs: W. Hamilton and J. A. Ibers, NUPIK, Picker input program; W. Hamilton, HORSE, general absorption program; R. Doedens and J. A. Ibers, NUCLS, least-squares program; A. Zalkin, FORDAP, Fourier program; W. Busing and H. Levy, ORFFE, function and error program; C. Johnson, ORTEP, thermal ellipsoid plot program; local data processing programs.

[5] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

TABLE I

FINAL ATOMIC PARAMETERS[a] FOR $[Pt(NH_3)_4]_2[Re_2O_3(CN)_8]$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt_1	0	0	0	0.00438 (4)	0.00569 (6)	0.00990 (9)	0	0.00464 (5)	0
Pt_2	0	0	$^1/_2$	0.00472 (4)	0.00654 (6)	0.00653 (8)	0	0.00363 (5)	0
Re	0.42719 (3)	0	0.09185 (4)	0.00369 (3)	0.00459 (4)	0.00703 (6)	0	0.00385 (4)	0
O_1	$^1/_2$	0	0	0.0049 (7)	0.0058 (10)	0.0100 (15)	0	0.0063 (10)	0
O_2	0.3615 (6)	0	0.1718 (9)	0.0057 (6)	0.0080 (8)	0.0143 (13)	0	0.0077 (8)	0
N_1	0.1650 (7)	0	0.2159 (11)	0.0047 (7)	0.0071 (10)	0.0091 (14)	0	0.0033 (9)	0
N_2	0.0782 (8)	0	0.9023 (12)	0.0058 (8)	0.0141 (16)	0.0140 (18)	0	0.0072 (11)	0
N_3	0.1636 (7)	0	0.5596 (10)	0.0043 (7)	0.0091 (12)	0.0083 (13)	0	0.0037 (8)	0
N_4	0	0.2164 (9)	$^1/_2$	0.0061 (7)	0.0061 (10)	0.0104 (14)	0	0.0043 (9)	0
N_5	0.6057 (5)	0.2476 (7)	0.3299 (8)	0.0071 (6)	0.0087 (8)	0.0091 (10)	--0.0014 (6)	0.0045 (7)	−0.0024 (8)
N_9	0.7550 (6)	0.2279 (7)	0.1755 (8)	0.0063 (5)	0.0067 (8)	0.0114 (11)	−0.0009 (5)	0.0049 (7)	−0.0007 (8)
C_1	0.5477 (6)	0.1595 (7)	0.2469 (9)	0.0048 (5)	0.0060 (8)	0.0090 (10)	−0.0000 (5)	0.0048 (7)	−0.0001 (8)
C_5	0.6884 (5)	0.1532 (7)	0.0744 (8)	0.0040 (5)	0.0044 (7)	0.0083 (10)	−0.0000 (5)	0.0036 (6)	−0.0007 (7)

[a] Standard deviations from the least-squares refinement are included in parentheses in this and subsequent tables.

3σ, where $\sigma = [\sigma^2_{\text{counting}} + (0.04F_o^2)^2]^{1/2}$. These 1729 reflections were used to determine and refine the structure.

Determination and Refinement of the Structure.—From a three-dimensional Patterson synthesis the platinum and rhenium atoms were located. A knowledge of the expected Re–O–Re distance aided in the distinction of Re from Pt. Since no significant difference in intensity of selected Friedel's pairs was observed, the space group $C2/m$ was assumed. This choice was subsequently verified by the refinement. Symmetry considerations place both Pt atoms in unrefineable fixed positions since each is located at the intersection of a mirror plane and a twofold axis. The bridging oxygen has the same symmetry requirements. Three of the four independent NH_3 nitrogens and the terminal oxygen were found to lie in the mirror plane. The fourth NH_3 nitrogen is situated on the twofold axis. The rhenium atoms are also on mirror planes but have refineable x and z coordinates. After refining the rhenium positions a three-dimensional Fourier synthesis was used to locate all the other nonhydrogen atoms. The scattering factor tables used for Pt and Re were those of Cromer and Waber,[6] while the anomalous scattering effects for these elements were from Cromer.[7] The N and C scattering factor tables were taken from Ibers[8] and for hydrogen those of Stewart, Davidson, and Simpson[9] were used. The anomalous scattering effects were included in F_c in the refinements.[10] Least-squares refinement of these nonhydrogen atoms with isotropic temperature factors minimizing the function $\Sigma w(|F_o|^2 - |kF_c|^2)^2$ converged with $R_1 = \Sigma(||F_o|^2 - |kF_c|^2|)/\Sigma|F_o|^2 = 0.081$ and $R_2 = [\Sigma w(|F_o|^2 + |kF_c|^2)^2/\Sigma w(|F_o|^2)^2]^{1/2} = 0.142$. In the above functions the weight $w = 1/\sigma^2$ where $\sigma = [\sigma^2_{\text{counting}} + (pF_o^2)^2]^{1/2}$. Several least-squares cycles with anisotropic thermal parameters and an isotropic extinction parameter[11] gave rapid convergence to the agreement factors $R_1 = 0.049$ and $R_2 = 0.081$. At this point the structure factors were examined, and the strong reflections were found to be underweighted. To correct for this the value of p in the standard deviation equations was changed from 0.04 to 0.025. Two additional cycles of refinement gave $R_1 = 0.048$ and $R_2 = 0.074$ with the standard deviation of an observation of unit weight being 1.39. No atomic parameter shifted by as much as 1.5σ as a result of this weighting change.

A difference Fourier synthesis based on this refinement allowed at least one hydrogen per amine group to be located. The remaining hydrogens were put in chemically reasonable positions in keeping with space group $C2/m$. This requires disorder of the hydrogens of N_4. With the hydrogen parameters fixed and with their isotropic temperature factors equal to 5, two additional least-squares cycles yielded $R_1 = 0.046$ and $R_2 = 0.071$. The conventional agreement factor $R = \Sigma(||F_o| - |kF_c||)/\Sigma|F_o|$ was 0.032. A final difference Fourier synthesis was carried out as a check on the correctness of the structure. The highest residual peaks were found near the rhenium and showed an electron density of 2.3 $e^-/\text{Å}^3$. The highest residual not associated with one of the heavy metals was 0.9 $e^-/\text{Å}^3$.

Although the agreement factors obtained above seemed to justify the refinement in the centrosymmetric space group $C2/m$, this space group imposes a great deal of symmetry on the molecule. So further refinement was attempted in $C2$ and in Cm after shifting the atoms away from the symmetrical configuration. In the noncentrosymmetric space group $C2$, 143 parameters were refined for several cycles (*vs.* 92 in $C2/m$). No improvement was found in the agreement factors and the atom positions oscillated about the centrosymmetric positions. Since convergence was not obtained, the application of Hamilton's R factor ratio test[12] was not possible. Attempted refinement in space group Cm was also unsuccessful.

The observed and calculated structure factors (×10) appear only in the microfilm edition of this journal.[13] The final atom positional and thermal parameters are presented in Table I.

Results

The structure consists of discrete planar $Pt(NH_3)_4^{2+}$ ions and distorted octahedral binuclear $ORe(CN)_4ORe(CN)_4O^{4-}$ ions (Figure 1). The latter has, within experimental error, a linear OReOReO arrangement (179.5 (8)° for OReO). The cyanide ligands on the two rhenium atoms of the binuclear ion are nearly eclipsed. The possibility of either C or N bonding of the cyanide ion was checked by a refinement of the isocyanide structure. The final agreement factors (without H's) were $R_1 = 0.052$ and $R_2 = 0.080$ compared with $R_1 = 0.048$ and $R_2 = 0.074$ for the carbon-bonded arrangement. The isocyanide arrangement also resulted in a considerably larger thermal vibration for the nitrogen atom directly bonded to the rhenium atom than for the terminal carbon atom. In the carbon-bonded refinement the terminal nitrogen atom of the cyano group had the greater thermal vibration which is physically reasonable. Thus the carbon-bonded structure is the most consistent with the data.

Alternate tetraammineplatinum(II) ions along the z axis are perpendicular to each other. The NH_3 hydrogens are involved in weak hydrogen bonding with the cyanide ion nitrogens and the terminal rhenium oxygens (Figure 2).

The bond distances and angles for the two ions are given in Tables II and III. The rms displacements from the thermal ellipsoids are given in Table IV. The shorter interionic, hydrogen-bond distances are presented in Table V.

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[6] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

[7] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[8] J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

[9] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[10] J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

[11] W. H. Zachariasen, *ibid.*, **16**, 1139 (1963).

[12] W. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964, p 158.

[13] This listing will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

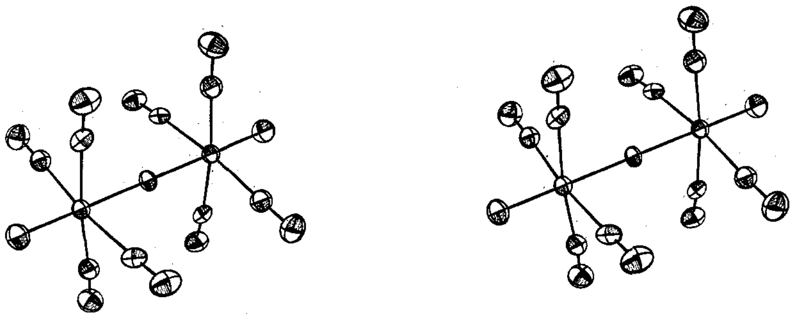

Figure 1.—Stereoscopic view of $ORe(CN)_4ORe(CN)_4O^{4-}$ showing thermal ellipsoids.

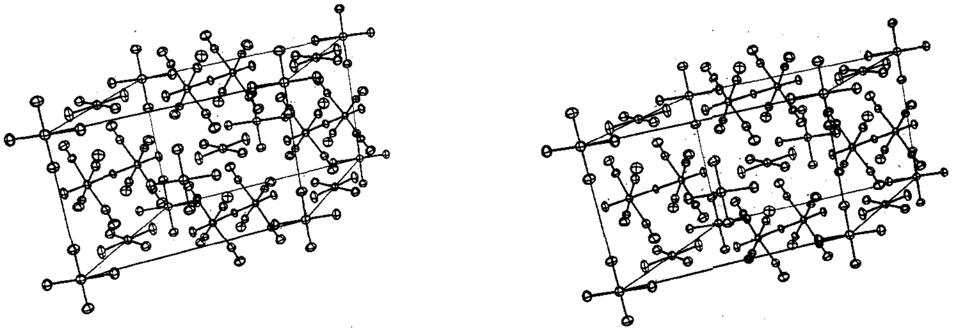

Figure 2.—Stereoscopic view of unit cell contents showing thermal ellipsoids.

Table II

Bond Distances and Bond Angles in $Pt(NH_3)_4^{2+}$

Distance	Value, Å	Angle	Value, deg
Pt_1–N_1	2.050 (9)	N_1–Pt_1–N_2	89.2 (4)
Pt_1–N_2	2.047 (9)	N_1–Pt_1–N_1'	180.0^a
Pt_2–N_3	2.049 (8)	N_3–Pt_2–N_4	90.0^a
Pt_2–N_4	2.059 (9)	N_4–Pt_2–N_4'	180.0^a

^{a} Fixed by symmetry.

Table III

Bond Distances and Bond Angles in $Re_2O_3(CN)_8^{4-}$

Distance	Value, Å	Angle	Value, deg	Angle	Value, deg
Re–O_1	1.9149 (4)	Re–O–Re	180.0^a	C_1–Re–C_2	91.2 (4)
Re–O_2	1.698 (7)	O_1–Re–O_2	179.5 (8)	C_1–Re–C_5	174.0 (3)
Re–C_1	2.124 (7)	O_1–Re–C_1	88.8 (2)	C_1–Re–C_6	90.5 (3)
Re–C_5	2.115 (7)	O_1–Re–C_5	85.5 (2)	C_5–Re–C_6	87.1 (4)
C_1–N_5	1.130 (9)	O_2–Re–C_1	91.5 (3)	Re–C_1–N_5	175.0 (6)
C_5–N_9	1.137 (9)	O_2–Re–C_5	94.2 (3)	Re–C_5–N_9	175.2 (6)

^{a} Fixed by symmetry.

Table IV

Rms Components of Thermal Displacement along the Principal Axes (Å)

Atom	Axis 1	Axis 2	Axis 3
Pt_1	0.156 (1)	0.162 (1)	0.193 (1)
Pt_2	0.153 (1)	0.173 (3)	0.177 (3)
Re	0.131 (1)	0.145 (1)	0.165 (1)
O_1	0.100 (20)	0.164 (15)	0.201 (14)
O_2	0.130 (12)	0.192 (11)	0.233 (11)
N_1	0.171 (14)	0.180 (13)	0.212 (13)
N_2	0.152 (15)	0.230 (15)	0.254 (14)
N_3	0.167 (12)	0.182 (13)	0.205 (13)
N_4	0.168 (14)	0.191 (12)	0.226 (13)
N_5	0.163 (11)	0.217 (11)	0.231 (9)
N_9	0.169 (10)	0.204 (9)	0.225 (10)
C_1	0.158 (10)	0.166 (10)	0.186 (10)
C_5	0.137 (11)	0.161 (9)	0.183 (10)

Table V

Selected Interionic Distances

Hydrogen bonds	Distance, Å	Hydrogen bonds	Distance, Å	Hydrogen, bonds	Distance, Å
N_1---O_2	3.248 (11)	N_3---N_5	3.216 (9)	N_3---N_9	3.228 (10)
N_2---O_2	3.215 (12)	N_4---N_5	3.178 (7)	N_4---N_9	3.065 (7)
N_1---N_5	3.104 (9)	N_1---N_9	3.077 (8)		

Discussion

The platinum atoms are each bonded in a square plane to four ammine groups with nearly equal Pt–N distances, 2.051 (9) Å. The N_1–Pt_1–N_2 angle, the only one not fixed by symmetry, is 89.2 (4)°. The same ion in $[Pt(NH_3)_4][PtCl_4]$ (Magnus' green salt) shows a Pt–N distance[14] of 2.06 Å while similar compounds (Table VI)[15–27] show a range from 2.02 to 2.06 Å.

The rhenium-containing anion has trans oxygens (Figure 3) which relates it to *trans*-$ReO_2(CN)_4^{3-}$ from which it was formed, and has an essentially linear ORe-OReO backbone. While this study was being completed, a similar arrangement was observed[19] in $Re_2O_3(S_2CN(C_2H_5)_2)_4$. A related molybdenum complex provides an example of the cis structure.[28] The terminal Re–O distance of 1.698 (7) Å is considerably shorter than that of the bridged oxygen, 1.9149 (4) Å. These values can be compared with the corresponding distances in $Re_2O_3(S_2CN(C_2H_5)_2)_4$ of 1.731, 1.738 and 1.920,

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(28) (a) R. N. Jowitt and P. C. Mitchell, *J. Chem. Soc. A*, 1702 (1970); (b) A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Amer. Chem. Soc.*, **86**, 3024 (1964).

TABLE VI

Bond	Distance, Å	Compound	Ref
Pt—N	2.051 (9)	$[Pt(NH_3)_4]_2$-$[Re_2O_3(CN)_8]$	. . .
	2.06 (6)	$[Pt(C_2H_5NH_2)_4]$-$[Pt(C_2H_5NH_2)_4Br_2]$-Br_4	15
	2.060 (25)	$[Pt(NH_3)_4]PtCl_4$ (Magnus' green salt)	14
	2.05 (20)	α-$Pt_2(SCN)_2Cl_2$-$(P(C_3H_7)_3)_2$	16
	2.02 (18)	*trans*-$Pt(C_2H_4)$-$((CH_3)_2NH)Cl_2$	17
Re—O (bridge)	1.9149 (4)	$[Pt(NH_3)_4]_2$-$[Re_2O_3(CN)_8]$	. . .
	1.860 (5)	$K_4Re_2OCl_{10} \cdot H_2O$	18
	1.901 (8), 1.920 (8)	$Re_2O_3(S_2CN(C_2H_5)_2)_4$	19
M—O (terminal)	1.698 (7)	$Re_2O_3(CN)_8^{4-}$	. . .
	1.781 (3)	$K_3[Re(CN)_4O_2]$	3
	1.834 (9)	$NaK_3Mo(CN)_4O_2 \cdot 6H_2O$	20
	1.77 (3)	$KReO_4$	21
	1.731 (8), 1.738 (8)	$Re_2O_3(S_2CN(C_2H_5)_2)_4$	19
	1.73 (6)	$((C_6H_5)_4As)[ReBr_4O$-$(CH_3CN)]$	22
	1.71 (4)	$((C_2H_5)_4N)[ReBr_4O$-$(OH_2)]$	23
M—C	2.124 (7), 2.115 (7)	$Re_2O_3(CN)_8^{4-}$	. . .
	2.130 (3), 2.139 (3)	$ReO_2(CN)_4^{3-}$	3
	2.220 (13), 2.189 (12)	$NaK_3Mo(CN)_4O_2 \cdot 6H_2O$	20
C≡N	1.130 (9), 1.137 (9)	$Re_2O_3(CN)_8^{4-}$	. . .
	1.154 (5), 1.156 (5)	$ReO_2(CN)_4^{3-}$	3
	1.150 (17), 1.186 (16)	$NaK_3Mo(CN)_4O_2 \cdot 6H_2O$	20
	1.155 (9)	$K_2Zn(CN)_4$	24
	1.06, 1.05, 1.16 (1)	KCN	25–27

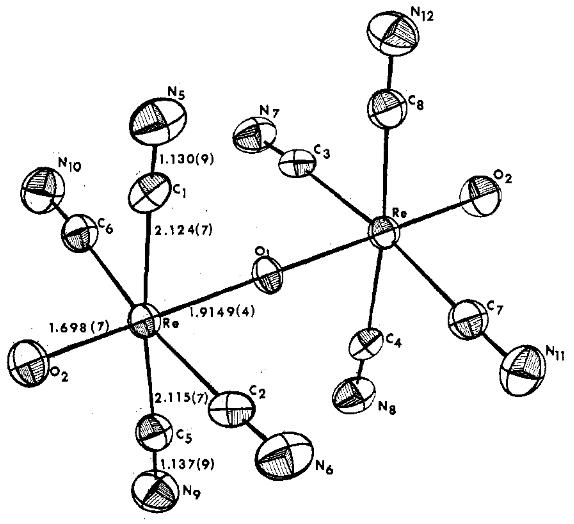


Figure 3.—Bond distances in $ORe(CN)_4ORe(CN)_4O^{4-}$: $C_1 = C_2 = C_3 = C_4$; $C_5 = C_6 = C_7 = C_8$; $N_5 = N_6 = N_7 = N_8$; $N_9 = N_{10} = N_{11} = N_{12}$.

1.901 Å, respectively. In Table VI are also listed some related bridged and terminal Re–O bond distances. For direct comparison the structure of the monomer $ReO_2(CN)_4^{3-}$ was recently reinvestigated[3] giving an Re–O distance of 1.781 (3) Å.

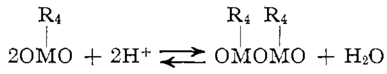
The cyano groups are carbon bonded which is normal for most metal complexes in the thermodynamically stable state and was also found for $ReO_2(CN)_4^{3-}$. It should be noted, however, that the structure of a nitrogen-bonded cyanide complex,[29] $K_2[ReN(NC)_4] \cdot H_2O$, of rhenium(V) has been reported. The C–N bond distances of 1.130 (9) and 1.137 (9) Å appear to be somewhat shorter than the latest values (Table VI) of about 1.16 Å (1.155 average) for $ReO_2(CN)_4^{3-}$, and the Re–C distances of 2.124 (7) and 2.115 (7) Å are about 0.01–0.02 Å shorter than in $ReO_2(CN)_4^{3-}$ (2.134 Å). The reason for these slight differences is not apparent.

The cyanide ions on the two rhenium atoms of the binuclear ion are essentially eclipsed (deviation 1.9 (2)° in the dihedral C–Re–O angles). This may imply appreciable π bonding in the bridge, which should be a maximum in the eclipsed configuration. However, in $Re_2O_3(S_2CN(C_2H_5)_2)_4$, the sulfur atoms are not eclipsed and yet a similar bridging Re–O distance is found. In this configuration π bonding should not be as effective but could still be a factor. The nearly eclipsed configuration and the deviation from it could also be due to hydrogen bonding with the NH_3 hydrogens and/or packing effects. Little interaction between CN groups occurs since N–N = 3.59 Å and C–C = 3.62 Å.

The interionic hydrogen bonding is weak as evidenced by the N(ammine)–N(cyanide) and N(ammine)–O(terminal) distances (Table V) of 3.07–3.23 and 3.22–3.24 Å, respectively. Such interactions would be expected to cause only minor deviations in the bond angles and distances in the rhenium and platinum complex ions. All other interionic distances are significantly longer than van der Waals contacts.

The thermal parameters (Tables I and IV) may be seriously affected by the high nonuniform absorption which is almost certainly not completely accounted for by the absorption corrections. The basic features of the thermal ellipsoids, however, appear to be physically reasonable with the maximum vibrations, in general, nearly perpendicular to the bonds. An interesting but unexplained feature is the vibration of the ammine nitrogens of the platinum cations. In both cations, alternating ammine nitrogens have their maximum vibration perpendicular to and in the square plane of the ion.

This X-ray crystal structure determination confirms the proposed structure of Toppen and Murmann[2] suggested by ^{18}O-exchange kinetic studies. Considering the ease of formation found and the number of oxygen atom bridged binuclear rhenium (and other 4+, 5+, and 6+ metal ions) complexes known, it appears that the reaction



$$2O\overset{R_4}{M}O + 2H^+ \rightleftharpoons O\overset{R_4}{M}O\overset{R_4}{M}O + H_2O$$

is fairly general for the trans dioxo complex ions. This dimerization may be compared with the well-known polymerization of CrO_4^{2-} in acidic media. Along these lines it should be pointed out that further polymerization to produce $OReO(-ReO)_nReO^{m-}$ ions in more acidic media is possible but so far has not been observed. A potential reason that further polymerization has not been observed is the necessarily weak multiple bonds which would be present for the internal OReO groups. Stabilization of the trimer and higher polymers may be obtained by equatorial ligands capable of ligand→metal π bonding which would provide another means of reducing the metal ion charge.

One can rationalize the Re–O, Re–C, and C–N distances in this ion using a bonding picture involving a strong multiple bond (approaching triple) of the terminal

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[29] W. O. Davies, N. P. Johnson, P. Johnson, and A. J. Graham, *Chem. Commun.*, 736 (1969).

oxygen to the metal ion with some π bonding M→CN with the cyanide ions. Multiple bonding to the bridging oxygen decreases the Re–O distance significantly below that for a single bond. On the basis of the small range of Re–O distances and the relative shortness of the bridged (single) Re–O bond compared with (single) Re–C distances we are of the opinion that all of the Re–O bonds seen here and in the other compounds in Table VI are stronger than single bonds and that none reaches pure triple-bond characteristics.

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The Crystal Structure of Triindenyluranium Chloride[1]

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The crystal structure of triindenyluranium chloride, $U(C_9H_7)_3Cl$, was determined from single-crystal X-ray diffraction data by use of Patterson and Fourier techniques and refined by the method of least squares to an R index of 0.047. The orthorhombic unit cell has $a = 8.576$ Å, $b = 14.24$ Å, $c = 16.73$ Å; the space group is $P2_12_12_1$; and $Z = 4$. In each molecule of the structure a uranium atom is bonded almost symmetrically to the carbon atoms of the five-membered ring of each of three planar indenyl ring systems at distances of 2.67–2.89 Å and to one chloride ion at 2.593 Å, in a tetrahedral array. Some types of bonding which are consistent with the observed molecular structure are discussed.

Introduction

A report on the preparation of triindenyluranium chloride,[3] $(C_9H_7)_3UCl$, raises the question of the type of bonding between the metal and the five-membered rings in this compound. While the similar cyclopentadienyl complexes with trivalent lanthanides and actinides are generally regarded as ionic,[4] there is evidence for a higher degree of covalency in organometallic complexes of the tetravalent actinides. Several compounds of uranium(IV) which have been described as having covalent bonding to some extent are $(C_5H_5)_3UCl$,[5] $(C_5H_5)_4U$,[6] $(C_3H_5)_4U$ (C_3H_5 = allyl),[7] and $(C_8H_8)_2U$ (C_8H_8 = cyclooctatetraenyl).[8] Structural investigation[9] of $(C_8H_8)_2U$ showed the existence of a π-sandwich complex similar to the well-known $(C_5H_5)_2Fe$, ferrocene.[10] For the case of $(C_5H_5)_3UCl$ an approximate determination,[11] in which individual carbon atoms were not located, showed the chlorine atom and the five-membered rings to be in a tetrahedral array about the uranium atom. This structure is consistent with either covalent or electrostatic attraction. The chemical evidence[5] for $(C_5H_5)_3UCl$ favors covalent bonding between the rings and uranium and ionic bonding between the chlorine and uranium.

Recently the structure of triindenylsamarium, $(C_9H_7)_3Sm$, was reported;[12] in it the metal is symmetrically bonded to the five-membered rings of three indenyl ring systems in a trigonal array. In contrast a covalent σ-type metal to carbon bond was proposed for $(C_9H_7)_3Sm \cdot THF$, based on nmr evidence.[13] No other lanthanide or actinide indenyl complexes have been reported, but the transition metal complexes $(C_9H_7)_2Fe$[14] and $(C_9H_7)_2Ru$[15] were both shown to have the sandwich-bond geometry.

The determination of the structure of triindenyluranium chloride, to be discussed here, was undertaken to provide accurate details from which the bonding possibilities can be considered. The naming of the compound which we use is not meant to imply any particular degree of covalency.

Experimental Section

The Sample.—The synthesis of triindenyluranium chloride is described elsewhere.[3] The compound crystallizes in the form of irregular polyhedra which are deep reddish brown and very reactive with moisture and air. For the X-ray diffraction study a crystal was chosen which had no well-defined faces but was approximately a prolate ellipsoid with major and minor axes of length 0.25 and 0.22 mm, respectively. It was sealed under vacuum in a thin-walled glass capillary tube.

Data Collection.—Precession X-ray photographs showed the orthorhombic symmetry, gave preliminary unit cell dimensions, and indicated the probable space group $P2_12_12_1$ by the pattern of systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$. For measurement of intensities the crystal was mounted on a computer-controlled Picker X-ray diffractometer which was equipped with a scintillation counter. Molybdenum Kα (Nb filtered) X-rays were employed at a takeoff angle of 2° and all independent reflections out to $2\theta = 55°$ were measured by θ–2θ scanning. The background was counted at the ends of each scan and the values were averaged. The length of scan ranged from 1° at the lower to 1.3° at the upper limit. The detector aperture was 3 mm. A reference reflection was measured once each hour; it usually varied by less than 2%

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