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Treatment of the Octachlorodirhenate Ion with High-pressure Carbon Monoxide; Preparation and Structure of [*cis*-$Re(CH_3CN)_4(CO)_2]_2[ReCl_6]$

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The reaction of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ *in acetonitrile with carbon monoxide at 100 atm and* ca. *90 °C gives several products, the major one being* $ReCl(CO)_5$. *One of the minor ones has been identified and characterized by X-ray crystallography as the ionic compound* [cis-$Re(CH_3CN)_4(CO)_2]_2[ReCl_6]$. *This compound forms monoclinic crystals in space group* $P2_1/c$ *with unit cell constants of:* a = *13.23(1)* Å; b = *10.092(7)* Å; c = *13.92(1)* Å, β = *112.18(6)°*; V = *1721(2)* Å^3; Z = *2. The cation has a distorted octahedral structure with the following distances: Re–C (av), 1.877(7)* Å; *Re–N (*trans *to CO), 2.134(9)* Å *and 2.156(10)* Å; *Re–N (*trans *to N), 2.052(9)* Å *and 2.072(9)* Å. *The* $[ReCl_6]^{2-}$ *anion resides on an inversion center and has Re–Cl distances of 2.367(3)* Å, *2.350(3)* Å *and 2.345(3)* Å.

Introduction

One of the most fascinating aspects of compounds with multiple M–M bonds [1] and perhaps one of their most important is their reactivity with small molecules such as CO, NO and with isocyanides and other organic molecules [1–4]. Reactions with strongly π-accepting ligands such as CO characteristically lead to scission of the M–M multiple bond and usually to the formation of mononuclear products. The ease of reaction varies considerably and in some cases it is necessary to employ higher than ambient temperatures and/or pressures.

The point of departure for the work reported here was an examination of the reactivity of CO under pressure towards the $[Re_2Cl_8]^{2-}$ ion on a small scale using a high-pressure cell [5, 6]. In this way the conditions under which a preparative scale reaction could be carried out were explored [6] and the infrared absorption bands of the various possible products were observed. Under all conditions tested, several products were formed and some were recognized as known compounds, *e.g.*, $ReCl(CO)_5$, which is the major product. One product that could not be so identified and that occurred as well-formed crystals was studied by X-ray crystallography and forms the subject of this paper. Its formula was found to be [*cis*-$Re(CH_3CN)_4(CO)_2]_2[ReCl_6]$. The acetonitrile is derived from the reaction solvent.

Experimental

Preparation

A solution of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$, 0.1 *M* in acetonitrile, was subjected 100 atm of CO at 90 °C for 8 h. The reaction mixture, cooled to room temperature and removed from the pressure vessel under argon, was found to consist of a white solid ($ReCl(CO)_5$ by IR) and a green solution. The green solution was separated by filtration, taken to dryness in vacuum and the residue placed on a silica gel column. Toluene eluted a yellow band (not yet identified) and tetrahydrofuran was then used to elute a bright green band. What appeared to be some unreacted starting material remained on the column. The green band eluted by THF was evaporated and the green solid redissolved in acetonitrile. On cooling to –20 °C a few small yellow crystals were formed and these were used for X-ray crystallographic characterization. The total yield of green material was about 20%. The major product, accounting for most of the remaining 80% of the rhenium, is $ReCl(CO)_5$.

X-ray Structure Determination[†]

A well-formed, regularly shaped crystal was mounted on a glass fiber and coated with a thin film

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[†] For footnote, see overleaf.

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TABLE I. Crystallographic Data.

Formula	$C_{20}H_{24}O_4N_8Re_3Cl_6$
Formula weight	1211.8
Space group	$P2_1/c$
a, Å	13.23(1)
b, Å	10.092(7)
c, Å	13.92(1)
β, degrees	112.18(6)
V, Å^3	1721(2)
Z	2
d_{calc}, g/cm^3	2.338
Crystal size, mm	0.1 X 0.1 X 0.2
μ(MoKα), cm^{-1}	111.76
Data collection instrument	Syntex P$\bar{1}$
Radiation	Mo Kα
Scan method	$\theta-2\theta$
Data collection range	4–50°
No. unique data, $F_o^2 \geqslant 3\sigma(F_o^2)$	1816
Number of parameters refined	187
R^a	0.0270
$R_w{}^b$	0.0378
Quality-of-fit indicator^c	0.896
Largest shift/esd, final cycle	<0.01

^{a}R = $\Sigma \| F_o| - |F_c\| / \Sigma |F_o|$. ^{b}R$_w$ = $[\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

of epoxy cement. Data were collected at 22 °C on a Syntex P$\bar{1}$ automated diffractometer with Mo Kα radiation monochromated with a graphite crystal. Least-squares refinement of 15 intense reflections in the range 20° < 2θ < 31° gave an orientation matrix from which was calculated setting angles and all parameters for a monoclinic cell. Systematic absences and successful refinement later showed the cell to belong to the space group $P2_1/c$. The $\theta-2\theta$ scan technique was used to measure intensities, with variable scan rates of 2.0–12.0°/min. Background measurements were made at both limits of each scan. Psi scans were taken on eight intense reflections so that an absorption correction could be applied. Crystallographic data are summarized in Table I.

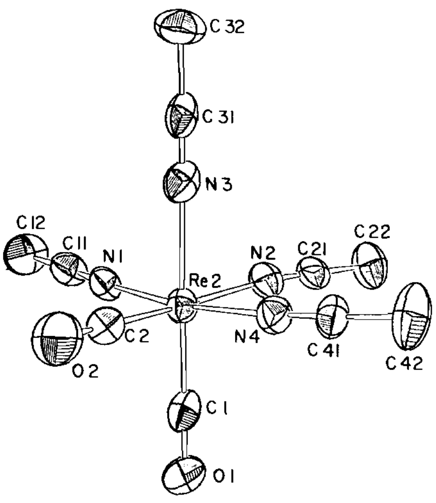

Fig. 1. The [*cis*-Re($CH_3CN)_4(CO)_2]^+$ ion, showing the atom labeling used in the tables.

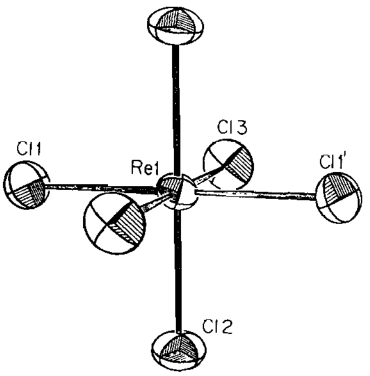

Fig. 2. The $[ReCl_6]^{2-}$ ion, which has crystallographic $\bar{1}$ symmetry.

Positional coordinates of the two Re atoms were taken from a three-dimensional Patterson map. Three cycles of isotropic least-squares refinement then gave discrepancy indices of R_1 = 0.134 and R_2 = 0.213. The remaining non-hydrogen atoms were located with subsequent least-squares cycles and difference Fourier maps, and refinement proceeded routinely to convergence with the final figures of merit being those given in Table I. The final positional parameters are listed in Table II; thermal parameters are available as supplementary material.

Results and Discussion

The compound we have studied, $[Re(CH_3CN)_4(CO)_2]_2[ReCl_6]$, is ionic and contains rhenium atoms in two oxidation states, +1 in the *cis*-[Re(CH$_3$-

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[†] General experimental and computing procedures were those commonly used in this Laboratory and frequently described in detail. Computing was done on a PDP 11/60 computer at B. A. Frenz, Associates, College Station, TX, U.S.A. using Enraf-Nonius Structure Determination Package of Frenz and Okaya.

TABLE II. Table of Positional Parameters and their Estimated Standard Deviations.[a]

Atom	*x*	*y*	*z*	*B* (Å^2)
Re1	0.000	0.500	0.000	2.55(1)
Re2	0.36800(3)	0.01789(3)	0.16604(3)	2.717(8)
Cl1	–0.0657(2)	0.4247(3)	0.1267(2)	3.91(6)
Cl2	0.1676(2)	0.3958(3)	0.0900(2)	4.15(6)
Cl3	0.0625(2)	0.6956(2)	0.0957(2)	4.42(7)
C1	0.6062(8)	0.6766(8)	0.3915(7)	3.4(2)
C2	0.5431(8)	0.4280(9)	0.3902(7)	3.7(2)
O1	0.4126(6)	0.2709(6)	0.0720(5)	4.7(2)
O2	0.4857(7)	0.3732(7)	0.4210(6)	6.3(2)
N1	0.2242(6)	–0.0198(7)	0.0410(5)	2.9(2)
N2	0.2725(6)	0.1152(7)	0.2411(5)	3.2(2)
N3	0.3352(6)	–0.1583(7)	0.2340(6)	3.4(2)
N4	0.4963(6)	0.0501(7)	0.3038(5)	3.2(2)
C11	0.1414(8)	–0.0415(9)	–0.0233(7)	3.5(2)
C12	0.0363(9)	–0.063(1)	–0.1062(8)	4.9(3)
C21	0.2317(8)	0.1769(9)	0.2856(6)	3.1(2)
C22	0.1772(8)	0.256(1)	0.3393(7)	4.5(3)
C31	0.3172(8)	–0.2519(9)	0.2696(7)	3.6(2)
C32	0.294(1)	–0.375(1)	0.3150(8)	5.5(3)
C41	0.5612(8)	0.0701(8)	0.3832(7)	3.4(2)
C42	0.646(1)	–0.909(1)	–0.5123(9)	5.5(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3) [$a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3)$ + ab(cos gamma)$\beta(1,2)$ + ac(cos beta)$\beta(1,3)$ + bc(cos alpha)$\beta(2,3)$].

TABLE III. Bond Distances and Bond Angles.[a]

A. The Cation, $[\textit{cis}\text{-Re(CH}_3\text{CN)}_4\text{(CO)}_2]^+$

Distances (Å)			
Re(2)–C(1)	1.879(11)	C(1)–O(1)	1.15(1)
Re(2)–C(2)	1.874(12)	C(2)–O(2)	1.15(1)
Re(2)–N(1)	2.072(9)	N(1)–C(11)	1.14(1)
Re(2)–N(2)	2.156(10)	N(2)–C(21)	1.15(1)
Re(2)–N(3)	2.134(9)	N(3)–C(31)	1.13(1)
Re(2)–N(4)	2.052(9)	N(4)–C(41)	1.13(1)
C(11)–C(12)	1.45(2)	C(31)–C(32)	1.48(2)
C(21)–C(22)	1.46(2)	C(41)–C(42)	1.48(2)
Angles (Deg.)			
C(1)–Re(2)–C(2)	89.5(5)	N(1)–C(11)–C(12)	177(1)
C(1)–Re(2)–N(1)	93.2(4)	N(2)–C(21)–C(22)	178(1)
C(1)–Re(2)–N(2)	93.0(4)	N(3)–C(31)–C(32)	179(1)
C(1)–Re(2)–N(3)	177.9(4)	N(4)–C(41)–C(42)	178(1)
C(1)–Re(2)–N(4)	92.5(4)		
C(2)–Re(2)–N(1)	94.7(4)		
C(2)–Re(2)–N(2)	176.0(4)		
C(2)–Re(2)–N(3)	92.7(4)		
C(2)–Re(2)–N(4)	92.2(4)		
N(1)–Re(2)–N(2)	88.3(3)		
N(1)–Re(2)–N(3)	86.8(3)		
N(1)–Re(2)–N(4)	171.1(3)		
N(2)–Re(2)–N(3)	84.9(3)		
N(2)–Re(2)–N(4)	84.5(3)		
N(3)–Re(2)–N(4)	87.3(3)		
Re(2)–C(1)–O(1)	177(1)		

(continued overleaf)

TABLE III. *(continued)*

Re(2)–C(2)–O(2)	177(1)
Re(2)–N(1)–C(11)	175.3(9)
Re(2)–N(2)–C(21)	172.1(9)
Re(2)–N(3)–C(31)	179.6(9)
Re(2)–N(4)–C(41)	174.5(9)
B. The Anion, $[ReCl_6]^{2-}$	
Distances (Å)	
Re(1)–Cl(1)	2.367(3)
Re(1)–Cl(2)	2.345(3)
Re(1)–Cl(3)	2.350(3)
Angles (Deg.)	
Cl(1)–Re(1)–Cl(2)	89.9(1)
Cl(1)–Re(1)–Cl(2)′	90.1(1)
Cl(1)–Re(1)–Cl(3)	89.8(1)
Cl(1)–Re(1)–Cl(3)′	90.2(1)
Cl(2)–Re(1)–Cl(3)	90.8(1)
Cl(2)–Re(1)–Cl(3)′	89.2(1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

$CN)_4(CO)_2]^+$ cation and +4 in the $[ReCl_6]^{2-}$ anion. The overall reaction leading to this compound, which is, as noted earlier, only a minor product, cannot be specified in detail. Broadly speaking, most of the Re^{III} in the $[Re_2Cl_8]^{2-}$ ion is reduced to Re^I and forms $ReCl(CO)_5$, liberating a great deal of Cl^-. Some of the Re^{III} presumably engages in a disproportionation reaction, giving Re^{IV} which combines with the available Cl^- to form $[ReCl_6]^{2-}$ while some Re^I forms $[Re(CH_3CN)_4(CO)_2]^+$ ions, incorporating CH_3CN molecules from the solvent.

The structure consists of a packing of cations and anions with no abnormal contacts. The cations occupy general positions and have no imposed crystallographic symmetry. In fact, they have C_{2v} (mm) symmetry within the experimental uncertainties. The bond distances and angles for both the cation and the anion (which resides on an inversion center) are listed in Table III.

The $[Re(CH_3CN)_4(CO)_2]^+$ ion has a slightly distorted octahedral structure, as would be expected for such an eighteen-electron species. While the C–Re–C angle in the *cis*-$Re(CO)_2$ moiety is 89.5(5)°, all the other angles that would be 90° in a regular octahedron deviate by *ca.* 3° from this value in the sense that all the CH_3CN ligands are shifted away from the CO ligands. The CO groups exert a marked structural *trans* effect, so that the Re–N bonds *trans* to CO groups are about 0.08 Å longer than the Re–N bonds that are *trans* to each other. The mean Re–CO distance, 1.877(7) Å, appears to be the shortest Re–CO distance known, although there are few accurate values available for comparison. While the positive oxidation number of +1 for the rhenium atom militates against extensive back-donation to π-accepting ligands, the fact that there are only two CO groups and the other four ligands are simple donors leads to a high degree of Re–C π bonding per CO ligand. In $ReCl(CO)_5$ [7] where the oxidation number of the metal atom is also +1 but there are five CO groups, the average Re–CO distance is 2.00(3) Å and even the shortest such bond, which is *trans* to the Cl atom, has a length of 1.91(1) Å. Even in the $[Re_4(CO)_{16}]^{2-}$ ion, where the mean oxidation number of the metal atoms is –½, the Re–CO distances range from 1.86(4) Å to 1.96(3) Å with an average value of 1.91 Å [8].

The only previously reported cation that is at all comparable to the *cis*-$[Re(CH_3CN)_4(CO)_2]^+$ ion is *fac*-$[Re(CH_3CN)_3(CO)_3]^+$, but this one has not, to our knowledge, been structurally characterized [9].

The $[ReCl_6]^{2-}$ anion resides on a center of inversion and is very nearly a regular octahedron. The average value of the angles between *cis* chlorine atoms is by symmetry exactly 90°; the six crystallographically independent values range from 89.2° to 90.8°. The three crystallographically independent Re–Cl distances have a mean value of 2.354(7) Å. The only previously reported value for this distance [10], 2.37 Å in cubic K_2ReCl_6, is not significantly different.

Acknowledgements

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Supplementary Material Available

Tables of anisotropic thermal parameters (3 pages) and a listing of observed and calculated structure factors (10 pages). They are available from FAC on request.

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