Crystal and Molecular Structure of Bromotricarbonyl(*NNN'N'*-tetramethylethane-1,2-diamine)rhenium(I)

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The crystal structure of the title compound has been determined from *X*-ray diffractometer data by the heavy-atom method. Crystals are monoclinic, space group $P2_1/n$ with a = 1 292.9(9), b = 1 474.2(6), c = 753.4(4) pm, β = 101.83(3)°, and Z = 4. The structure has been refined by block-diagonal least squares to R 0.075 for 1 699 observed reflections. The co-ordination geometry about rhenium is approximately octahedral with the bromine and tetramethylethane-1-2-diamine ligands mutually *cis*. The Re–Br bond is 263.6(2) pm long. The chelate ring is disordered and two crystallographically independent conformations are found for the molecule, differing in the way in which the carbon–carbon bond in the chelate ring bends to achieve an unstrained conformation.

IN the structural studies of rhenium carbonyl compounds reported to date the covalent radius of the Re atom has been calculated by halving the Re–Re distance in polynuclear rhenium carbonyls.[1-4] Doubts have been expressed as to the efficacy of this method for transition-metal atoms [5,6] and, in our recent investigation of silyl and polysilyl derivatives of rhenium carbonyl,[7] we were able to predict a maximum value for the radius of the formally rhenium(I) atom which was significantly less than the value so obtained. The present study examines the structure of bromotricarbonyl(*NNN'N'*-tetramethylethane-1,2-diamine)-rhenium(I) in an attempt to test this prediction in a situation where the presence of potential π-acceptor ligands other than carbon monoxide cannot affect the observed bond lengths.

EXPERIMENTAL

Preparation.—The title compound was prepared from bromopentacarbonylrhenium and *NNN'N'*-tetramethylethane-1,2-diamine (tmen) in diglyme by the method of Abel and Tyfield.[8] The compound recrystallised from hexane as colourless needles and was characterised by i.r.[8] and mass spectroscopy.

Crystal Data.—$C_9H_{16}BrN_2O_3Re$, M = 466.34, Monoclinic, a = 1 292.9(9), b = 1 474.2(6), c = 753.4(4) pm, β = 101.83°, U = 1.405 3 × 10^9 pm^3, D_m = 2.19(1) g cm^{-3}, Z = 4, D_c = 2.20 g cm^{-3}, $F(000)$ = 872, Mo-K_α radiation λ = 71.07 pm, μ = 121.46 cm^{-1}. Diffraction data were collected from a transparent needle-shaped crystal whose dimensions were 0.45 × 0.25 × 0.20 mm.

The crystal was found to be monoclinic on the basis of precession photography using Cu-K_α *X*-radiation and the space group was uniquely confirmed as $P2_1/n$ from the systematic absences, $0k0$ where $k = 2n + 1$ and $h0l$ where $h + l = 2n + 1$. Accurate lattice and orientation parameters were obtained from a least-squares refinement of the setting angles of 12 reflections centred in a circular receiving aperture (diameter 5 mm) set 23 cm from the crystal on a Hilger and Watts four-circle computer-controlled diffractometer. The mosaicity of the crystal was examined by means of open-counter ω scans at a take-off angle of 3°; the widths at half-height for intense low-angle reflections [9] ranged from 0.10 to 0.13°.

Zirconium-filtered Mo-K_α *X*-radiation and the θ—2θ scan technique were used to collect the intensities of 2 109 independent reflections in the quadrant $hk \pm l$ of reciprocal space for which $0 < 2\theta \leqslant 48°$. A symmetric scan range of 1.50° in 2θ, centred on the calculated peak position [λ(Mo-K_α) = 71.07 pm], was composed of 75 steps each of 0.8 s duration. Stationary crystal–stationary counter background counts of 15 s were measured at each end of the scan range. Where necessary, to bring reflections within the linear response range of the scintillation counter, attenuators were automatically inserted in the primary beam. Crystal stability was confirmed by the constancy of three reference reflections whose intensities were regularly monitored.

An initial correction for background was made and the standard deviation $\sigma(I)$ of the corrected intensity I was estimated in the manner previously described.[7] For the initial refinement, p was given the value 0.09 and is the factor included to avoid overweighting the more intense reflections. The intensities were then corrected for Lorentz and polarisation effects.

Of the 2 109 reflections collected, 1 699 had values of F_o^2 that were greater than three times their estimated standard deviations and it was these that were used in the final refinement.

Solution and Refinement of the Structure.—In the block-diagonal least-squares refinements the function minimised was $\Sigma[w(|F_o| - |F_c|)^2]$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes respectively, and $w = 4F_o^2/\sigma^2(F_o^2)$. The agreement factors R and R' are defined in the standard way.

The scattering-factor tables used for all atoms were calculated using the polynomial constants for HF SCF evaluated by Cromer and Mann.[10] The effects of anomalous dispersion of Re and Br atoms were included [11] in F_c using Cromer's [12] values for $\Delta f'$ and $\Delta f''$.

The positional parameters of the rhenium atom were obtained from an unsharpened three-dimensional Patterson synthesis. Refinement of these co-ordinates together with an isotropic temperature factor for this atom gave values of 0.304 and 0.400 for R and R' respectively. Two difference-Fourier syntheses revealed the co-ordinates of all the other non-hydrogen atoms. At this stage, the relatively large temperature factors for some of the atoms suggested disorder of the tmen group.

The data were reprocessed with p = 0.16, and corrections for crystal absorption were made. High values for the isotropic temperature factors suggested that anisotropic thermal models would be more appropriate for all atoms other than the carbon atoms associated with the co-ordinated tmen, and least-squares refinement of this model led to values for R and R' of 0.088 and 0.109 respectively.

Examination of the isotropic temperature factors for the carbon atoms of the disordered tmen group and an inspection of a difference-Fourier map in this region of the structure indicated that the disorder was caused by a superposition of two conformers of the chelate ring. Thus, the ring appeared almost planar, but the C–C bond distance was unrealistically short (121 pm). Two different and half-populated positions were then assigned to each of the atoms C(4), C(5), C(7), and C(9). The co-ordinates for these were obtained from close inspection of a difference-Fourier map. The refinement was then continued, with isotropic temperature factors for the disordered atoms and anisotropic factors for the other atoms, until convergence was reached with R and R' equal to 0.075 and 0.094 respectively.

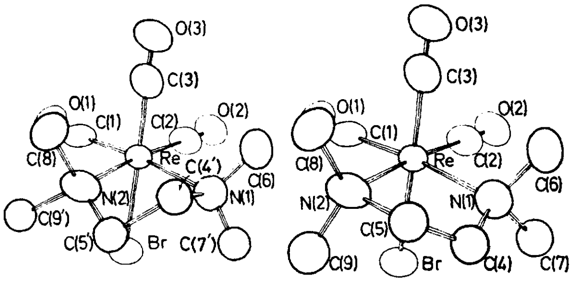

FIGURE 1 General view of the two conformers of the molecule $[ReBr(CO)_3(tmen)]$

A final difference-Fourier synthesis showed no anomalously high peaks. The relative weighting scheme appeared satisfactory since $\Sigma[w||F_o| - |F_c||^2]$ showed only a slight dependence on $|F_o|$ and $\lambda^{-1}\sin\theta$. The error in an observation of unit weight is 1.10 electrons. Structure-factor calculations for the **410** reflections having $F_o^2 < 3\sigma(F_o^2)$ revealed no anomalies of the type $|F_c| \gg |F_o|$. There was no evidence for secondary extinction.

The positional parameters obtained from the last cycle of refinement are listed in Table 1. Root-mean-square amplitudes of vibration for the atoms refined anisotropically, thermal parameters, and final observed and calculated structure factors are listed in Supplementary Publication No. SUP 22495 (6 pp.).*

TABLE 1

Final positional parameters for $[ReBr(CO)_3(tmen)]$

Atom	X	Y	Z
Re	0.208 4(1)	0.082 3(1)	−0.168 1(1)
Br	0.355 4(2)	−0.008 5(1)	−0.289 2(3)
O(1)	0.053(1)	−0.062(1)	−0.346(3)
O(2)	0.165(1)	0.196(1)	−0.511(2)
O(3)	0.032(1)	0.181(1)	−0.062(2)
N(1)	0.333(1)	0.180(1)	−0.021(3)
N(2)	0.255(1)	0.008(1)	0.101(2)
C(1)	0.111(1)	−0.013(1)	−0.279(3)
C(2)	0.182(1)	0.152(1)	−0.386(2)
C(3)	0.095(2)	0.144(1)	−0.098(3)
C(6)	0.293(2)	0.269(1)	0.007(4)
C(8)	0.167(2)	0.006(1)	0.200(3)
C(4)	0.395(4)	0.137(4)	0.119(7)
C(4′)	0.339(4)	0.143(3)	0.203(6)
C(5)	0.342(4)	0.083(3)	0.225(7)
C(5′)	0.358(3)	0.036(3)	0.189(5)
C(7)	0.402(3)	0.209(3)	−0.174(6)
C(7′)	0.427(3)	0.185(2)	−0.051(5)
C(9)	0.322(4)	−0.073(3)	0.105(7)
C(9′)	0.260(3)	−0.104(2)	0.062(5)

All calculations were carried out using a Burroughs 6712 computer. The data-processing program HILGOUT is based on DRED (J. F. Blount) and PICKOUT (R. J. Doedens). Numerical absorption corrections were applied using the program ABSORB which is a major modification of AGNOST (L. Templeton and D. Templeton). Structure-factor calculations and least-squares refinements were carried out using the program CUCLS and Fourier summations by use of FOURIER. These are highly modified versions of the well known programs ORFLS (W. A. Busing, K. O. Martin, and H. A. Levy) and FORDAP (A. Zalkin) respectively. Interatomic distances and angles and thermal-vibration analysis were obtained from the program ORFFE also by Busing *et al.* DANTEP, a modification of ORTEP by C. K. Johnson, was used for calculation of interatomic distances and angles and for production of structure diagrams on an incremental plotter.

RESULTS AND DISCUSSION

The crystal consists of discrete molecules, the shortest intermolecular distance (not involving H atoms) being **305** pm. The atom-numbering scheme is defined in Figure 1 which also shows the two conformers of the chelate ring. Table 2 lists selected bonded and non-bonded interatomic distances and Table **3** selected angles.

The overall geometry of the molecule shows the co-ordination of the rhenium atom to be approximately

TABLE 2

Selected bond distances (pm) for $[ReBr(CO)_3(tmen)]$

Re–Br	263.6(2)	N(1)–C(4)	135(2)
Re–C(1)	195(2)	N(1)–C(4′)	177(2)
Re–C(2)	191(2)	N(1)–C(7)	166(2)
Re–C(3)	189(2)	N(1)–C(7′)	129(2)
Re–N(1)	228(1)	N(2)–C(5)	170(2)
Re–N(2)	227(2)	N(2)–C(5′)	142(2)
C(1)–O(1)	109(2)	N(2)–C(9)	148(2)
C(2)–O(2)	113(2)	N(2)–C(9′)	168(2)
C(3)–O(3)	107(2)	C(4)–C(5)	140(7)
N(1)–C(6)	144(3)	C(4′)–C(5′)	160(6)
N(2)–C(8)	149(2)		

TABLE 3

Selected angles (°) for $[ReBr(CO)_3(tmen)]$

Re–C(1)–O(1)	176(2)	Re–N(1)–C(6)	114(1)
Re–C(2)–O(2)	176(2)	Re–N(1)–C(7)	105(1)
Re–C(3)–O(3)	178(2)	Re–N(1)–C(7′)	123(2)
		Re–N(1)–C(4)	109(2)
Br–Re–C(1)	86.1(5)	Re–N(1)–C(4′)	99(2)
Br–Re–C(2)	89.3(5)		
Br–Re–C(3)	175.5(5)	Re–N(2)–C(8)	112(1)
Br–Re–N(1)	90.2(5)	Re–N(2)–C(9)	117(2)
Br–Re–N(2)	89.2(5)	Re–N(2)–C(9′)	109(1)
		Re–N(2)–C(5)	102(2)
N(1)–Re–N(2)	80.6(6)	Re–N(2)–C(5′)	110(2)
N(1)–Re–C(1)	173.4(6)		
N(1)–Re–C(2)	93.5(6)	C(6)–N(1)–C(7)	98(1)
N(1)–Re–C(3)	93.8(8)	C(6)–N(1)–C(7′)	111(2)
N(2)–Re–C(1)	93.9(7)	C(6)–N(1)–C(4)	119(2)
N(2)–Re–C(2)	173.9(6)	C(6)–N(1)–C(4′)	95(2)
N(2)–Re–C(3)	93.5(7)	C(7)–N(1)–C(4)	110(3)
		C(7)–N(1)–C(4′)	109(2)
C(1)–Re–C(2)	91.9(9)		
C(1)–Re–C(3)	90.1(6)	C(8)–N(2)–C(9)	118(2)
C(2)–Re–C(3)	88.4(6)	C(8)–N(2)–C(9′)	97(1)
		C(8)–N(2)–C(5)	103(2)
N(1)–C(4)–C(5)	116(4)	C(8)–N(2)–C(5′)	121(2)
C(4)–C(5)–N(2)	113(4)	C(9)–N(2)–C(5)	101(2)
N(1)–C(4′)–C(5′)	103(3)	C(9′)–N(2)–C(5′)	108(2)
C(4′)–C(5′)–N(2)	100(3)		

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

octahedral with the tmen ligand forming a chelate ring. The stereochemistry is *facial*, with the bromine atom and the nitrogen-donor atoms of the diamine mutually *cis*. This is in keeping with the observation of three strong carbonyl-stretching absorptions ($2A' + A''$) in the i.r. spectrum of the molecule.[8]

The Re–Br bond length in $[ReBr(CO)_3(tmen)]$ is found to be **263.6(2)** pm, slightly longer than the **262(1)** pm observed in $[ReBr(CO)_5]$.[13] Subtraction of the Pauling covalent radius for the bromine atom (114 pm) [14] from the Re–Br internuclear separation in either of these molecules gives values for the covalent radius of the Re(I) atom in the range **148—150** pm. These values are close to that predicted from our studies on rhenium–silicon systems [7] but are somewhat less than the 151—152 pm obtained by halving the Re–Re bond lengths in polynuclear rhenium carbonyl compounds.[1-4] The difference in values obtained by the two methods is considerably smaller for rhenium than in the corresponding manganese system, where halving the Mn–Mn distance in $[Mn_2(CO)_{10}]$ predicts a manganese radius some 8 pm greater than the currently accepted value.[15] Effects such as repulsion between non-bonding electrons on the adjacent metal atoms [16] are clearly attenuated on progressing down the transition-metal series.

Although the errors in Re–C distances are large, the mean Re–CO distance in $[ReBr(CO)_3(tmen)]$ [192(2) pm] is significantly shorter than those found in $[ReBr(CO)_5]$,[13] $[Re_2(CO)_{10}]$,[1] or $[Re(SiR_3)(CO)_5]$.[7] This may be attributed to a redistribution of *d*-electron density over the three carbonyl groups following replacement of two carbonyl ligands by the σ-donating tmen. Surprisingly, the mean C–O distance [110(2) pm] is somewhat shorter than is usual for rhenium carbonyl systems.

The tmen ring was found to be disordered and refinement was successfully completed by giving equal occupancy factors to two sets of co-ordinates for the ethylene carbon atoms, C(4) and C(5), and two of the methyl carbons C(7) and C(9). Errors in the bond lengths and angles for the disordered tmen ligand are high but the values appear unexceptional when compared with those for other transition-metal compounds of tmen,[17-21] although to our knowledge this represents the first reported structure of a tmen derivative of a metal carbonyl compound. Indeed, crystallographic data for nitrogen compounds of transition metals in low oxidation states are relatively scarce. This necessitated extrapolations from the small amount of available data for strain-energy calculations of nitrogen-chelate compounds of metal carbonyls.[22]

TABLE 4

Puckering of the ethanediamine rings for $[ReBr(CO)_3(tmen)]$ *

Plane defined by atoms	Atom	Deviation (pm) from plane	Angle/°	
			α	β
Re,N(1),N(2)	C(4)	42	23.5	51.4
	C(5)	13		
	C(4′)	51	39.9	74.5
	C(5′)	52		

* α is the angle between the N–Re–N plane and the C–Re–C plane, β the torsion angle between the N atoms across the C–C bond [see Figure 2(*b*) and ref. 23].

The disorder in the tmen ring can be described in terms of the rotation about the two N–Re bonds [Figure 2(*a*)] resulting in the observation of the two *gauche* conformations of the chelate rings designed as δ and λ respectively.[23,24] Table 4 lists the dihedral angles α between the plane containing the rhenium and ring-carbon atoms and that which contains the ring-nitrogen atoms and the metal. The fact that these angles are non-zero confirms the *gauche* configuration of both conformers.[23] The angles β [Figure 2(*b*)] between the two nitrogen atoms looking down the C–C bond of the ethanediamine ring are also given. Similar disorder involving the tmen ligand has been observed in the structure of a number of lithium compounds of tmen by Stucky and co-workers.[25-28] The barrier to conformational interconversion in solution has been obtained for a small number of octahedral [22,29] and tetrahedral [30] compounds of tmen from lineshape analyses of the low-temperature ^1H and ^{13}C n.m.r. spectra. These results together with strain-energy minimisation calculations [22] indicate that the barrier to conformational interconversion is significantly greater for tmen than unsubstituted ethanediamine chelates, and may be critically dependent on the M–N bond length. Further work is in progress in these laboratories to investigate the effect of both N–N bond length and apical-ligand substitution on the conformational barriers of rhenium and manganese compounds of tmen.

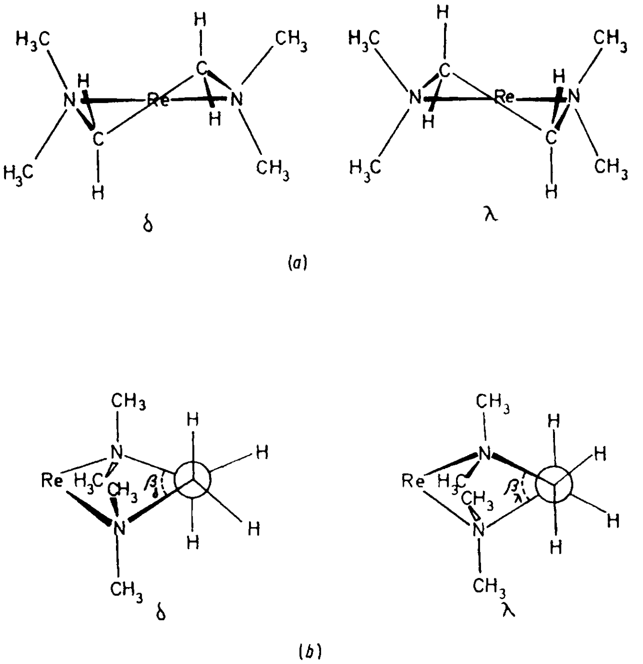

FIGURE 2 (*a*) The two *gauche* conformers, δ and λ, of the Re(tmen) ring; (*b*) *gauche* conformations of the Re(tmen) ring showing the β angles (for a definition of β see footnote to Table 4)

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