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REACTIONS OF COORDINATED MOLECULES

XXXIV *. THE CRYSTAL AND MOLECULAR STRUCTURE OF [*fac*-$(OC)_3Re(CH_3CO)_3$]BBr AND FURTHER REFINEMENT OF THE MOLECULAR STRUCTURE OF [*fac*-$(OC)_3Re(CH_3CO)_3$]BCl

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Summary

The X-ray molecular structural determinations of [*fac*-$(OC)_3Re(CH_3CO)_3$]BX, where X is Cl or Br, are reported. Both structures reveal that the triacetylrhenato ligand acts as a trioxygen, vicinal, bifurcated chelating ligand of ca. C_{3v} symmetry when coordinated to a boron atom. Further refinement of the chloride structure using a non-unitary intensity weighting scheme affords smaller estimated standard deviations and a slightly asymmetrical, localized electronic structure within the tridentate rhenato ligand. The structure of the bromide complex, as determined from a larger data set than that used for the chloride compound, indicates a symmetrical coordination of the triacetylrhenato ligand.

Introduction

We reported previously the preparation of the triacetyltricarbonylrhenato dianion, [*fac*-$(OC)_3Re(CH_3CO)_3]^{2-}$, and its coordination to aluminum(III) and hafnium(IV) affording anionic and neutral bis-chelate, octahedral complexes, respectively [2]. A subsequent report demonstrated a general preparation of *fac*-triacyltricarbonylrhenato dianions and confirmed their coordination to metal ions as tridentate, chelating ligands of idealized C_{3v} symmetry by observing the predicted geometrical isomerism when one of the acyl ligands is unique [3].

Reaction of the triacetyltricarbonylrhenato dianions with the boron trihalides affords the neutral complexes, [*fac*-$(OC)_3Re(CH_3CO)_3$]BX, where X is F, Cl, Br or I [4]. These complexes were apparently the first examples of known boron complexes containing trioxygen, vicinal, bifurcated chelating ligands. The tripodal coordination

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* For Part XXXIII see ref. 1.

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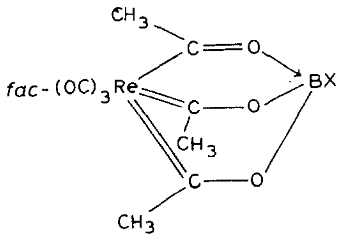
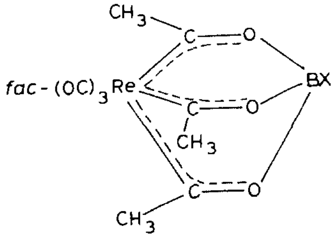
geometry of the triacetyltricarbonylrhenato ligand was confirmed by X-ray diffraction of the crystalline boron chloride complex [5]. However, crystal decomposition during X-ray data collection on this compound afforded relatively large estimated standard deviations (esd's) which prevented a detailed examination of the electronic structure within the triacylrhenato ligand.

This paper reports; (1) further refinement of the molecular structure of [*fac*-$(OC)_3Re(CH_3CO)_3]BCl$ (I) by using a non-unitary intensity weighting scheme for the X-ray reflections which gives smaller esd's than those reported earlier, and (2) a complete X-ray crystal and molecular structural determination of the analogous bromide complex, [*fac*-$(OC)_3Re(CH_3CO)_3]BBr$ (II). Determination of the precise molecular structures of these most simple triacylrhenato complexes is relevant to the elucidation of the bonding within these rhena-triacylmethanide ligands. These ligands could act as either unsymmetrical, tripodal ligands, such as III, or symmetrical, tripodal ligands, like IV. Structural type III has a localized electronic structure consisting of two formal carbenoid ligands and one acetyl ligand, while structural type IV has a symmetrical, delocalized π-electron distribution within the three acetyl ligands. The analysis of these structural data is summarized below.



(III)



(IV)

Results and discussion

Further refinement of the structure of [fac-$(OC)_3Re(CH_3CO)_3]BCl$ (I)

The X-ray structure of I has been reported previously [5]. The molecular structure was most consistent with the localized electronic structure III rather than the delocalized structure IV as indicated by comparing interatomic distances. Relatively large esd's on bond distances and angles resulted from a unitary weighting scheme for all reflections and a 25 percent decrease in standard reflection intensities during data collection due to crystal decomposition. A correction for changes in intensity of the standard reflections was made, however.

To improve the statistical treatment of these data, the intensity weighting scheme was changed from a refinement using unitary weights to one which includes the measured standard deviation on the intensity [6]. Refinement under these conditions was successful also under space-group symmetry $P2_1/m$ with $Z = 2$. As before, refinement under $P2_1$ symmetry did not converge.

Refinement with a more statistically correct weighting scheme reduced average bond distance and bond angle esd's by ca. 25 and 20 percent, respectively, and the R factors, R and R_w, improved, respectively, from 0.099 to 0.069 and from 0.084 to 0.064. An ORTEP diagram of I was reported previously [5]. The atomic numbering

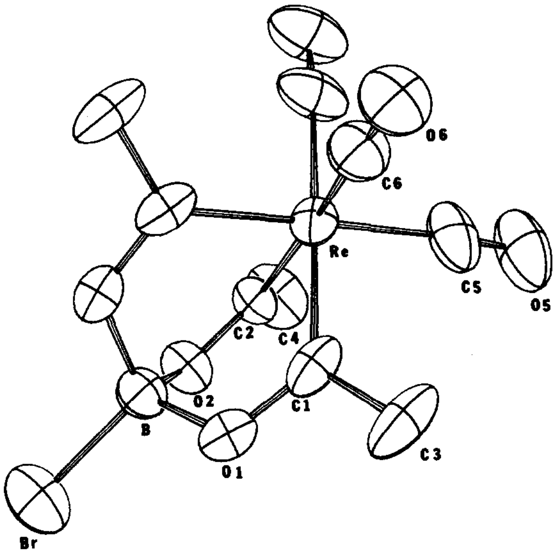


Fig. 1. An ORTEP diagram of [*fac*-$(OC)_3Re(CH_3CO)_3$]BBr (ellipsoids at 30% probability) showing the atomic numbering scheme.

TABLE 1

COMPARISON OF SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) (with esd's) FOR [*fac*-$(OC)_3Re(CH_3CO)_3$]BCl (I)

	Ref. 5	This work		Ref. 5	This work
Re–C(1)	1.93(3)	1.93(2)	C(2)–C(4)	1.50(5)	1.48(4)
Re–C(2)	2.10(4)	2.10(3)	C(1)–O(1)	1.42(4)	1.42(3)
Re–C(5)	1.75(5)	1.81(4)	C(2)–O(2)	1.23(5)	1.31(3)
Re–C(6)	1.99(4)	1.97(3)	B–O(1)	1.47(3)	1.46(2)
C(5)–O(5)	1.27(6)	1.18(4)	B–O(2)	1.47(4)	1.45(3)
C(6)–O(6)	1.16(5)	1.18(4)	B–Cl	1.81(4)	1.83(3)
C(1)–C(3)	1.52(4)	1.53(3)	O(1)–O(2)	2.39(3)	2.38(2)
C(1)–Re–C(2)	83(2)	84.0(8)	Re–C(6)–O(6)	178(4)	176(3)
C(1)–Re–C(5)	90(2)	90(1)	Re–C(1)–C(3)	137(3)	135(2)
C(1)–Re–C(1)′ [a]	87(2)	85.5(9)	Re–C(1)–O(1)	122(2)	124(2)
C(1)–Re–C(5)′	175(2)	175(2)	Re–C(2)–C(4)	122(3)	129(2)
C(2)–Re–C(5)	93(2)	92(2)	Re–C(2)–O(2)	124(3)	120(2)
C(2)–Re–C(6)	170(2)	170(2)	C(4)–C(2)–O(2)	114(3)	110(2)
C(2)–Re–C(1)′	83(2)	84.0(8)	C(3)–C(1)–O(1)	102(3)	101(2)
C(2)–Re–C(5)′	93(2)	92(2)	C(1)–O(1)–B	116(2)	114(2)
C(5)–Re–C(6)	94(2)	94(2)	C(2)–O(2)–B	117(3)	117(2)
C(5)–Re–C(1)′	175(2)	175(2)	O(1)–B–O(2)	109(2)	110(2)
C(5)–Re–C(5)′	94(2)	93(2)	O(1)–B–O(1)′	110(2)	112(2)
C(6)–Re–C(1)′	89(2)	89(1)	O(1)–B–Cl	111(2)	109(2)
C(6)–Re–C(5)′	94(2)	94(2)	O(2)–B–O(1)′	109(2)	107(2)
C(1)′–Re–C(5)′	90(2)	91(2)	O(2)–B–Cl	108(2)	107(2)
Re–C(5)–O(5)	174(4)	173(3)	O(1)′–B–Cl	111(2)	109(2)

[a] Primed atoms are generated by the symmetry operation: x, $(1/2 - y)$, z.

scheme is identical to that shown in Fig. 1 for the corresponding bromide complex. A comparison of selected interatomic distances and angles with esd's under each refinement scheme are shown in Table 1.

The molecular structure of I is still described best as a localized structure III at both the $\pm 2\sigma$ and $\pm 3\sigma$ limit. The Re–C(2) acyl distance of 2.10(3) Å is larger than the two symmetry equivalent rhenium–carbon acyl distances Re–C(1) and Re–C(1)′ of 1.93(2) Å even at a $\pm 3\sigma$ significance. The acetyl ligand containing C(2) is unique in that it lies in the crystallographic mirror plane. The uniqueness of this acetyl ligand is evident also from the shorter acetyl C(2)–O(2) distance of 1.31(3) Å as compared to the corresponding equivalent C(1)–O(1) and C(1)′–O(1)′ distances of 1.42(3) Å. In the formal structure III, the C(2) acyl ligand is acting as the acetyl ligand, while the C(1) and C(1)′ acyl ligands represent the equivalent formal carbenoid ligands. The C(2) acyl ligand exerts a more pronounced *trans*-effect on the diametrically opposite Re–CO distance, also. The Re–C(6) distance of 1.97(3) Å is significantly longer than the equivalent Re–C(5) and Re–C(5)′ distances of 1.81(4) Å at better than a $\pm 2\sigma$ level. The three B–O distances are not significantly different, however, and are consistent with a pseudotetrahedral coordination geometry about the boron atom. The average value of the O–B–O angles is 110(3)° with range from 107(2) to 112(2)°.

The atoms C(1) and C(1)′ have unusually large thermal motion approximately normal to the plane defined by C(1), C(1)′ and C(2), while the thermal ellipsoid of C(2) is nearly spherical (principal axes values are 5.6, 7.4 and 5.1). Presumably, there is a disorder in the C(1) and C(1)′ positions corresponding to a "rocking" vibration of the chelate frame which pivots about C(2).

Crystal and molecular structure of [fac-$(OC)_3Re(CH_3CO)_3$]BBr (II)

Because II has comparable stability to that of I, an X-ray structural determination of II was undertaken to hopefully avoid extensive crystal decomposition during data collection. Although the intensities of standard reflections decreased by 29 percent during the X-ray data collection of II, the amount of data collected is nearly twice that amount of data collected for I, thereby affording a more precise determination of the atomic positions of II. The crystalline structure of II is isomorphous to that of I. Refinement of II was successful under $P2_1/m$ symmetry, but was not successful under $P2_1$ symmetry (as found with I, also).

The crystal structure of II consists of discrete molecules. The atomic numbering scheme and a perspective view of the molecule are provided in Fig. 1. An intermolecular H... H distance of 2.562(1) Å is the shortest such contact, and this represents a normal Van der Waals contact distance. Selected interatomic distances and angles are compiled in Table 2, and selected least-squares plane data are listed in Table 3. Values of interatomic distances and angles are rounded in the usual fashion, while the standard deviations for these values are always rounded to the next larger digit.

Because of crystal decomposition during data collection care must be exercised in the interpretation of the data. Although the extent of crystal decomposition during data collection of II is comparable to that encountered to I, the atomic positions of II are determined more precisely than those of I, because the number of reflections collected for II is 1741 compared to only 988 reflections for I.

Within a $\pm 2\sigma$ limit, the complex exhibits idealized C_{3v} symmetry. The molecule has crystallographically-imposed mirror symmetry, and the dihedral angle between

TABLE 2

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) (with esd's) FOR [*fac*-$(OC)_3Re(CH_3CO)_3$]BBr (II)

Re–C(1)	2.03(2)	C(2)–C(4)	1.50(3)
Re–C(2)	2.06(2)	C(1)–O(1)	1.39(2)
Re–C(5)	2.07(2)	C(2)–O(2)	1.31(3)
Re–C(6)	2.02(3)	B–O(1)	1.47(2)
C(5)–O(5)	1.08(3)	B–O(2)	1.55(3)
C(6)–O(6)	1.13(3)	B–Br	1.91(3)
C(1)–C(3)	1.51(2)	O(1)–O(2)	2.43(2)
C(1)–Re–C(2)	82.9(5)	Re–C(6)–O(6)	172(3)
C(1)–Re–C(5)	95.6(7)	Re–C(1)–C(3)	128(2)
C(1)–Re–C(1)′[a]	85.5(6)	Re–C(1)–O(1)	122.7(9)
C(1)–Re–C(5)′	174.9(6)	Re–C(2)–C(4)	131(2)
C(2)–Re–C(5)	92.3(6)	Re–C(2)–O(2)	107(2)
C(2)–Re–C(6)	167.9(9)	C(4)–C(2)–O(2)	107(2)
C(2)–Re–C(1)′	82.9(5)	C(3)–C(1)–O(1)	110(2)
C(2)–Re–C(5)′	92.3(6)	C(1)–O(1)–B	117(2)
C(5)–Re–C(6)	94(2)	C(2)–O(2)–B	117(3)
C(5)–Re–C(1)′	174.9(6)	O(1)–B–O(2)	107(2)
C(5)–Re–C(5)′	82.9(8)	O(1)–B–O(1)′	112(2)
C(6)–Re–C(1)′	88.2(7)	O(1)–B–Br	111(1)
C(6)–Re–C(5)′	96.7(8)	O(2)–B–O(1)′	107(1)
C(1)′–Re–C(5)′	95.6(7)	O(2)–B–Br	108(2)
Re–C(5)–O(5)	176(2)	O(1)′–B–Br	111(1)

[a] Primed atoms are generated by the symmetry operation: x, $(1/2-y)$, z.

planes I and II is 118.2° which is close to the expected value of 120°.

The rhenium atom exhibits nearly octahedral coordination geometry with average values for the angles defining the principal coordination axes and for the angles between adjacent ligands being 173(1) and 89(1)°, respectively. However, atoms C(5) and C(5)′ lie 0.12 Å from plane III, while atom C(6) lies 0.30 Å from plane VI, thus indicating an actual lower symmetry about the rhenium atom.

The three rhenium–carbon acyl distances, Re–C(1) and Re–C(1)′ of 2.03(2) Å and Re–C(2) of 2.06(2) Å, are equivalent within a $\pm 1\sigma$ level of confidence, as are the three rhenium–carbonyl carbon distances, Re–C(5) and Re–C(5)′ of 2.07(2) Å and Re–C(6) of 2.02(3) Å.

A slightly lower molecular symmetry is evident in the three acyl carbon–oxygen distances, C(1)–O(1) and C(1)′–O(1)′ of 1.39(2) Å and C(2)–O(2) of 1.31(3) Å, and the three boron-oxygen distances, B–O(1) and B–O(1)′ of 1.47(2) Å and B–O(2) of 1.55(3) Å. However, the individual distances within each type of bond are equivalent within a $\pm 2\sigma$ limit. Therefore, in contrast to the structure of I, the chemical bonding within the unique C(2) acetyl ligand of II is not significantly different from that of the other two mirror-related acetyl ligands within a $\pm 2\sigma$ confidence level.

The thermal motion of acyl carbons, C(1) and C(1)′, methyl carbons, C(3) and C(3)′, and acyl oxygens, O(1) and O(1)′, is directed ca. normal to the plane defined by C(1), C(1)′ and C(2), while the atoms of the unique C(2) acetyl ligand exhibit little excessive distortion in this direction. However, this directed thermal motion is less pronounced than is found in the corresponding atoms of molecule I.

TABLE 3

SELECTED LEAST-SQUARES PLANES[a] AND ATOMIC DEVIATIONS FROM THE PLANES FOR [*fac*-$(OC)_3Re(CH_3CO)_3$]BBr (II)

Atom	Deviation (Å)	Atom	Deviation (Å)
Plane I: $1.7795 \times 10^{-5}I + 1.0000J + 4.2791 \times 10^{-6}K = 2.2630$			
Re[b]	−0.0000		
C(2)[b]	0.0000		
C(2)[b]	0.0000		
B[b]	−0.0000		
Plane II: $0.8321I - 0.4718J + 0.3162K = 1.8820$			
Re[b]	−0.0025	C(2)	1.4112
C(1)[b]	0.0060	C(1)′[c]	−1.2908
O(1)[b]	−0.0068	O(2)	1.2782
B[b]	0.0033	O(1)′	−1.1545
Plane III: $0.6401I - 8.9875 \times 10^{-4}J + 0.7683K = 2.4831$			
Re[b]	0	C(5)	0.1781
C(1)[b]	0	C(5)′	0.1781
C(1)′[b]	0		
Plane IV: $0.9506I + 5.5095 \times 10^{-5}J + 0.3104K = 2.4831$			
C(1)[b]	−0.0000		
O(1)[b]	0.0000		
C(1)′[b]	0.0000		
O(1)′[b]	−0.0000		
Plane V: $-0.8428I + 3.7354 \times 10^{-5}J + 0.5382K = 1.5651$			
B[b]	0		
O(1)[b]	0		
O(1)′[b]	0		
Plane VI: $-0.5915I + -0.7297J + 0.3431K = 0.8833$			
Re[b]	0	C(6)	0.2880
C(1)[b]	0	C(5)′	−0.0602
C(2)[b]	0		
Plane VII: $-0.4468I + 0.8610J = 0.2427K = -0.7189$			
C(1)′[b]	−0.0047	C(3)	−0.6757
O(1)[b]	0.0052	C(4)	−0.7230
O(2)[b]	−0.0055		
Plane VIII: $7.4307 \times 10^{-2}I - 0.4975J + 0.8674K = 3.5041$			
B[b]	0		
O(1)[b]	0		
O(2)[b]	0		

[a] Equations of the planes are expressed as $PI + QJ + RK = S$ in orthogonal Ångstrom space (see text for angles of intersecting planes). [b] Atoms used in calculating planes. [c] Primed atoms generated by the symmetry operation x, $(1/2 - y)$, z.

Overall, the structures of I and II differ significantly in four bond distances and three bond angles. Within the mirror-related acyl ligands, the Re–C(1) distances and the C(3)–C(1)–O(1) angles for I and II are 1.93(2) vs. 2.03(2) Å and 101(2) vs. 110(2)°, respectively. Within the carbonyl ligands, the Re–C(5)–C(5)′ angles and the Re–C(5) and C(5)–O(5) distances for I and II are 93(2) vs. 82.9(8)°, 1.81(4) vs. 2.07(2) Å, and 1.18(4) vs. 1.08(3) Å, respectively. The B–O(2) distances of I and II are 1.45(3) and 1.55(3) Å, respectively.

Conclusion

Within a $\pm 3\sigma$ limit, the chloride complex I has an essentially localized structure (like III), while the bromide complex II has an essentially delocalized structure (like IV) within a $\pm 2\sigma$ limit. The reason for this structural difference between I and II is not known, although the relatively poor quality of the diffraction data precludes a more detailed analysis of the chemical bonding within I and II. Based on better quality structural determinations of metalla-β-diketonato complexes which contain two symmetrical chelating acyl ligands [7], a symmetrical, delocalized structure for these triacylrhenato ligands might be expected. Complex II, which is the structure of better quality, is in agreement with this expectation. Structural differences between I and II due to subtle electronic differences are possible also.

Experimental

Further refinement of the structure of [fac-$(OC)_3Re(CH_3CO)_3$]BCl (I)

The details of data collection and preliminary corrections applied to the data have appeared elsewhere [5]. To better describe the data statistically, the intensities were weighted by a scheme modeled after that described by Hughes [6]; weight = $1/(J)$, where (J) is the larger of σ or 0.0001 and σ is the measured standard deviation of the intensity.

Atomic parameters for all atoms were assigned values from the previous study. All non-hydrogen atoms were refined anisotropically. Isotropic methyl hydrogens were approximated by six equally-spaced and appropriately-weighted hydrogen atoms, located tetrahedrally 1.0 Å from the carbon position. The final R factor was 0.069 and the weighted R factor was 0.064. The maximum shift-to-error ratio for the atomic parameters in the final cycle was 0.49. The maximum electron density on the final difference map was 1.6 eÅ^{-3}, located near Re. Atomic parameters and a listing of observed and calculated structure factors are available from the principal author upon request.

Refinement of the atomic parameters was attempted under space group $P2_1$ without convergence. Temperature factors on C(1) and C(5) failed to refine, with the temperature factors approaching nonpositive-definite values both isotropically and anisotropically.

Crystal and molecular structure of [fac-$(OC)_3Re(CH_3CO)_3$]BBr (II)

Pale yellow crystals of II were prepared [4] and crystallized from hexane at −20°C. Collection of the X-ray data, polarization and absorption corrections, including a correction for intensity changes on the standard reflections were performed by Molecular Structure Corporation, College Station, Texas, as a commercial, technical service.

A needle-shaped crystal of II having dimensions 0.2 × 0.2 × 0.3 mm was mounted in a glass capillary with its long axis roughly parallel to the φ axis of the goniometer. Preliminary examination and data collection were performed with Mo-K_α radiation (λ 0.71073 Å) on an Enraf–Nonius CAD4 computer controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochrometer.

Cell constants were obtained from the refinement of 25 reflections. The monoclinic cell parameters and calculated cell volume are: a 7.148(3), b 9.052(2), c

11.194(4) Å, β 99.35(3)°, V 714.7 Å^3. The calculated density for two molecules per unit cell ($Z = 2$) and mol. wt. 490.02 is thus 2.28 g cm^{-3}. Systematic absences indicated the space groups $P2_1$ or $P2_1/m$.

The data were collected at 23 ± 1°C using the ω–θ scan technique. The scan rate varied from 2 to 20°/min (in ω), utilizing a slow scan rate on weak reflections to assure good counting statistics. Data were collected to a maximum 2θ of 55.0°. The scan width was calculated as follows: scan width = ω scan width = $0.8 + 0.35(\tan \theta)$. Background counts were made by scanning an additional 25 percent above and below this range.

Intensities and standard deviations on intensities were calculated using the formulae: $I = S(C - RB)$ and $(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$; where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count and p is a factor introduced to downweight intense reflections and was set to 0.05.

A total of 1814 reflections were collected, of which 1741 were unique and not systematically absent. As a check on crystal stability, three standard reflections were measured periodically, showing an intensity loss of 29 percent during data collection. An anisotropic decay correction was applied. The correction factors on intensity ranged from 1.001 to 1.403 with an average of 1.164. Relative transmission coefficients ranged from 0.82 to 1.00 with and average value of 0.92.

Since II is isomorphous to I, its chloride analogue, refined positional and thermal parameters for I served as input for the full least-squares refinement of this molecule. Methyl hydrogen atoms were approximated by six equally spaced and appropriately weighted H atoms, located tetrahedrally 1.0 Å from the carbon position.

The final refinement was carried out with all non-hydrogen atoms anisotropic and with the isotropic hydrogens included but not refined. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F_o)$. Atomic scattering factors for the neutral atoms were those tabulated by Cromer and Mann [8] except for hydrogen where Stewart's values [9] were used. The anomalous dispersion factors for all atoms except hydrogen were those given by Cromer and Liberman [10]. The final R factor was 0.079 and the weighted R factor, R_w, was 0.076. The maximum shift-to-error ratio for the atomic parameters on the final cycle was 0.019. The maximum electron density on the final difference map was 2.8 eÅ^{-3} near Re. The atomic parameters and a listing of observed and calculated structure factors are available from the principal author upon request.

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