to reflux for periods as long as 2 days. No apparent reaction occurred, and this was confirmed by ^{1}H NMR spectroscopy of the solids obtained from stripping the solution to dryness.

Attempted Comproportionation Reactions Involving $M(O\text{-}i\text{-}Pr)_5$ (M = Nb, Ta) and $Mo_2(O\text{-}i\text{-}Pr)_6$ or $Wo(O\text{-}i\text{-}Pr)_2(HNMe_2)_2$. Stoichiometric amounts of the reagents $M(O\text{-}i\text{-}Pr)_5$ (M = Nb, Ta) and $Mo_2(O\text{-}i\text{-}Pr)_6$ or $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ (ca. 200–300 mg) were dissolved together in 10–20 mL of hexane. The solutions were allowed to stir at room temperature for as long as 4 days or heated at reflux for as long as 2 days. No apparent reaction occurred, and this was confirmed by ^{1}H NMR spectroscopy of the solids obtained from stripping the solution to dryness.

Crystallographic Studies. General operating procedures and listings of programs have been given previously.[7] Crystal data are summarized in Table IV.

$W_3O(O\text{-}i\text{-}Pr)_{10}$ and $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$. Preliminary examination of the samples indicated that they were isomorphous with $Mo_3O(O\text{-}i\text{-}Pr)_{10}$. The mixed-metal complex is undoubtedly disordered with respect to the location of the metal atoms, and so no data were taken other than for the cell parameters (−159 °C): $a = 21.324$ (13) Å, $b = 21.874$ (14) Å, $c = 10.235$ (5) Å = 98.79 (3)°, $\beta = 92.77$ (3)°, $\gamma = 117.85$ (2)°.

Data were collected in the usual manner for the $W_3O(O\text{-}i\text{-}Pr)_{10}$ sample, and the starting coordinates for the $Mo_3O(O\text{-}i\text{-}Pr)_{10}$ sample were used. Because of the number of atoms involved in the refinement, no attempt was made to include hydrogen contributions.

A final difference Fourier synthesis was featureless, with several peaks of 0.9–1.3 e Å^{-3} located in the vicinity of the six tungsten atoms. Scans indicated no absorption correction was necessary.

Acknowledgment. We thank the Office of Naval Research and the Wrubel Computing Center for support.

Registry No. $W_3O(O\text{-}i\text{-}Pr)_{10}$, 92562-31-7; $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$, 92562-32-8; $MoW_2O(O\text{-}i\text{-}Pr)_{10}$, 93862-15-8; $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$, 84028-40-0; $WO(O\text{-}i\text{-}Pr)_4$, 93862-16-9; $Mo_2(O\text{-}i\text{-}Pr)_6$, 62521-20-4; $MoO(O\text{-}i\text{-}Pr)_4$, 79210-24-5; $W(NPh)(O\text{-}i\text{-}Pr)_4$, 93842-63-8; $Nb(O\text{-}i\text{-}Pr)_5$, 18368-80-4; $Ta(O\text{-}i\text{-}Pr)_5$, 16761-83-4; Mo, 7439-98-7; W, 7440-33-7.

Supplementary Material Available: Listings of a comparison of bond distances and bond angles for the $M_3O(O\text{-}i\text{-}Pr)_{10}$ molecules (M = Mo and W) and anisotropic thermal parameters, complete listings of bond distances and angles, figures showing the atom number scheme, and a table of observed and calculated structure amplitudes for $W_3O(O\text{-}i\text{-}Pr)_{10}$ (83 pages). Ordering information is given on any current masthead page.

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Molecular Structure of Monomeric Cobalt Dibromide with Some Information on the Structure of the Dimer from Electron Diffraction

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Received June 6, 1984

As part of our research on the molecular structure of transition-metal dihalides, an electron diffraction investigation of vapor-phase cobalt dibromide has been carried out. Several first-row transition-metal dichlorides ($MnCl_2$,[3] $FeCl_2$,[4] $CoCl_2$[5]) and dibromides ($MnBr_2$,[6] $FeBr_2$,[4] $NiBr_2$[7]) have already been investigated in our Budapest laboratory. In addition to the determination of the geometrical parameters and mean vibrational amplitudes of the monomers, their bending vibrational frequencies have also been estimated. The presence of a small amount of dimeric species has also been detected in the manganese dibromide and iron dibromide experiments, and a limited amount of structural information has been gained on these species as well.

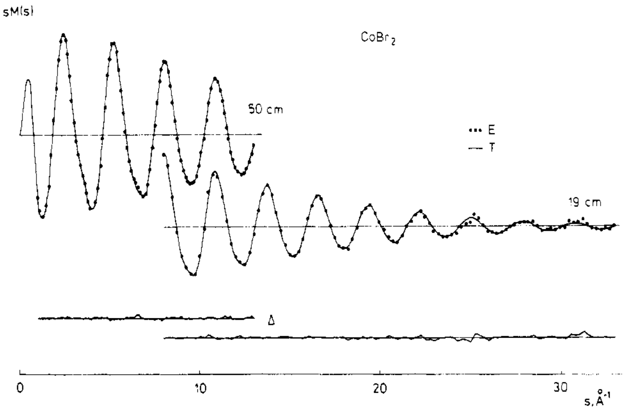

Figure 1. Experimental (E) and theoretical (T) molecular intensities, the latter for a model of 94% monomer and 6% dimer.

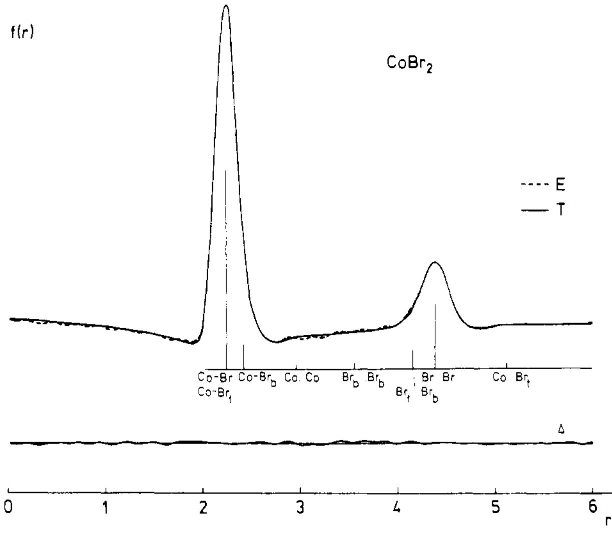

Figure 2. Radial distribution curves, corresponding to the molecular intensities of Figure 1.

Experimental Section

The sample of cobalt dibromide was a commercial product (Ventron 23149). Due to the low volatility of cobalt dibromide, relatively high-temperature conditions had to be used in the electron-scattering experiment. The composition of the vapors of transition-metal halides may be complicated, especially at high temperatures. Therefore, the combined electron diffraction/quadrupole mass spectrometric technique developed in our laboratory[8] was utilized. The choice of the nozzle material is also of importance as indeed some metals used for the nozzle showed reactions with the sample in the preliminary experiments. Finally, a molybdenum nozzle was used. The recorded mass spectra showed no indication of any reaction products in the experiments with this nozzle. However, the presence of a small amount, about 5%, of dimeric species was indicated at the electron diffraction experimental conditions.

The necessary vapor pressure for the electron diffraction experiment could be reached at a nozzle temperature of 635 °C. The so-called radiation nozzle[3] was used. All other experimental conditions, the data processing, and the source of the scattering functions were the same as in the other studies in this series.[3-7]

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Table I. Structural Parameters for Cobalt Dibromide (Estimated Total Errors Given in Parentheses as Units in the Last Digit)[a]

	Monomer		
r_g(Co–Br)	2.241 (5) Å	ν_1	212 (20) cm^{-1}
l(Co–Br)	0.079 (2) Å	ν_2	68 (8) cm^{-1}
κ(Co–Br)	1.95 × 10^{-5} (40) Å^3	ν_3	396 (10) cm^{-1} [b]
r_g(Br···Br)	4.387 (9) Å	rel monomer amt	94.2 (7)%
l(Br···Br)	0.130 (4) Å		
δ_g(Br···Br)	0.095 (10) Å		
	Dimer		
r_g(Co–Br$_t$)	2.241 (5) Å[c]	r_g(Co–Br$_b$)	2.429 (14) Å
l(Co–Br$_t$)	0.080 (2) Å	l(Co–Br$_b$)	0.110 Å[d]

[a] For error estimation of the distances and amplitudes, see: Hargittai, M.; Hargittai, I. *J. Chem. Phys.* **1973**, *59*, 2513. In estimation of the error limits of the frequencies, all uncertainties of the input parameters have been taken into account. [b] Taken from experiment.[13] [c] Assumed to be identical with the monomer bond distance. [d] The difference of the two bond amplitudes was constrained.

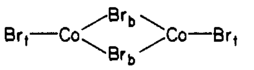
The molecular intensities and the radial distribution curves are shown in Figures 1 and 2.

Results and Discussion

The main features of the radial distribution curve correspond to the cobalt dibromide monomeric molecules. Some slight discrepancies occur, however. They can be interpreted as originated from a small amount of dimeric species. This interpretation is consistent with the mass spectra and with experience on other dibromides (see above).

The structural parameters determined by a least-squares procedure based on the molecular intensities are collected in Table I. The parameters of the monomer and the monomer/dimer ratio were stable in all refinements and proved to be insensitive to various assumptions about the dimer structure. On the other hand, excluding the presence of dimeric species considerably changed the parameters obtained for the monomer (viz., r_g(Co–Br) = 2.25 Å, κ(Co–Br) = 4.35 × 10^{-5} Å^3, δ(Br···Br) = 0.126 Å) and considerably worsened the agreement between experimental and calculated distributions.

Because of the small relative abundance in the vapor, the complete geometry of dimeric cobalt dibromide could not be determined. Earlier spectroscopic studies[9-11] as well as our electron diffraction results on other dibromides showed a four-membered ring structure compatible with the experiment:



This model fits the experimental data for cobalt dibromide as well. Although the point group of the equilibrium structure may be D_{2h}, implying a planar ring, a considerably puckered ring structure is deduced from the electron diffraction data. Both terminal bonds appear to be in equatorial positions; thus, the apparent point group is C_{2v}. This symmetry lowering in the electron diffraction structure is typical for molecules performing low-frequency, large-amplitude vibrations.

This is observed for the monomer as well. The Br···Br nonbonded distance is considerably shorter than twice the Co–Br bond length as obtained directly from the electron diffraction data. As these are thermal average distances,[12] this shrinkage may again be a consequence of low-frequency, large-amplitude bending vibrations.

An earlier gas-phase spectroscopic investigation[13] suggested that cobalt dibromide is linear, indeed, similar to many other dihalides in the first transition-metal series.

Assuming linearity, the observed shrinkage effect provides a possibility for estimating the ν_2 bending vibrational frequency from the diffraction data. In principle all three vibrational frequencies of a linear triatomic molecule could be determined from electron diffraction data. There are three parameters in the electron diffraction structure analysis directly related to molecular vibrations (viz., the two mean parallel vibrational amplitudes, l(Co–Br) and l(Br···Br), and the shrinkage, δ). However, because of the small harmonic vibration approximation and assumptions of parallel and perpendicular displacements of atoms in the normal-coordinate analysis,[14] the calculation relating the vibrational frequencies and the other vibrational parameters may lead to erroneous results. It is mainly the vibrational amplitude of the nonbonded distance that is effected by these approximations, while the other two parameters, namely the vibrational amplitude of the bond distance and the shrinkage, are quite well reproduced by the conventional normal-coordinate calculations.[15]

The ν_3 antisymmetric stretching frequency of cobalt dibromide was determined by gas-phase infrared spectroscopy.[13] This frequency and the l(Co–Br) and δ(Br···Br) parameters from electron diffraction were used to predict the other two vibrational frequencies. They are given in Table I.

The geometrical parameters and the estimated vibrational frequencies for the monomer follow the trends observed for other first-row transition-metal dihalides.[6,16] The bond length variation of the dibromides is similar to that of the dichlorides: the bond lengths decrease from the manganese dihalides toward the nickel dihalides. The available bending vibrational frequencies of first-row transition-metal dihalides are below 100 cm^{-1}, with those of the dibromides being about 10–20 cm^{-1} smaller than those of the corresponding dichlorides. All these bending vibrational frequencies are, however, considerably larger than suggested by earlier predictions.[17]

Registry No. $CoBr_2$, 7789-43-7; Co_2Br_4, 94136-82-0.

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