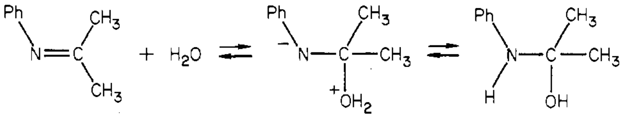
has been discussed extensively. Kalinowski and Kessler[19] have reviewed the subject. Three major mechanisms have been considered: (a) polarization of C=N to C^+—N^- followed by rotation about the C—N bond, (b) inversion about the nitrogen giving a linear C=N—C transition state, and (c) the formation of an intermediate carbonyl amine. The last mechanism can be directly eliminated for the present catalyzed reactions by the observation that exchange of CH_3 with CD_3 is much faster than exchange with CH_2D. For the uncatalyzed reaction, the weight of the evidence favors the nitrogen inversion mechanism[19] b. Among the evidence quoted in support of this conclusion is the observation that formation of a complex between the imine and aluminum trimethyl completely inhibits isomerization.[20] The rate of the uncatalyzed reaction is increased by electron-withdrawing substituents on the nitrogen. That of catalyzed reaction is dramatically increased by electron-donating substituents on the nitrogen. Clearly a different mechanism is involved. Complexation to the metal ion is strongly suggested. Electron-donor substituents will increase the Lewis basicity of the imine nitrogen and favor complexation to a metal ion. Such complexation will prevent inversion but will favor C—N rotation by polarization of the bond. A rotation mechanism is therefore indicated for the catalyzed process.

Complexation to a metal ion will clearly reduce the C=N bond order and facilitate rotation. Attack by a nucleophile to give a carbinolimine type of intermediate will accomplish the same end, e.g.



The most reasonable interpretation of the above results would seem to be that both metal complexation and nucleophilic attack are necessary to bring about isomerization. The term in the rate equation proportional to aniline concentration represents the effect of aniline as a nucleophile, i.e., transimination. The term independent of aniline could well represent the contribution of other nucleophiles, i.e., solvent (acetonitrile), water, anil, and thiourea, present in the solution.

This interpretation is consistent with our previous mechanistic conclusions concerning anil hydrolysis and transimination. The rate-determining step in these reactions is the rate of attack of a nucleophile (water or aniline) held in the second coordination sphere of the catalytic complex on anil coordinated to the metal ion. The rate of isomerization is greater than either anil hydrolysis or transimination because it is determined by the sum of the rates for all the nucleophiles present including probably solvent molecules which cannot react with the anil to give a new product.

Acknowledgment. The authors are indebted to the National Science and Engineering Research Council of Canada for financial support of this research.

Registry No. $Zn(tu)_4(ClO_4)_2$, 19596-77-1; *N*-isopropylideneaniline, 1124-52-3; *N*-isopropylidene-*p*-toluidine, 39058-29-2; *N*-isopropylidene-*p*-anisidine, 40938-34-9; *N*-isopropylidene-*p*-fluoroaniline, 51678-96-7; *N*-isopropylidene-*p*-chloroaniline, 40938-43-0; *N*-isopropylidene-*p*-bromoaniline, 40938-44-1; *N*-isopropylidene-*m*-nitroaniline, 22104-23-0; *N*-isopropylidenebenzylamine, 1197-48-4.

---

(19) Kalinowski, H. O.; Kessler, H. *Top. Stereochem.* **1973**, *7*, 295.
(20) Jeffery, E. A.; Meisters, A.; Mole, T. *Tetrahedron* **1969**, *25*, 741.

Contribution from the Department of Chemistry,
University of Delaware, Newark, Delaware 19711

Structure and Bonding in Chloro- and Bromobismuthate(III) Clusters (BiX_4^-, $Bi_2X_9^{3-}$, BiX_6^{3-}) by NQR Spectroscopy

A. G. LANDERS and T. B. BRILL*

Received July 8, 1979

The structural aspects of difficultly characterized halobismuthate(III) salts have been probed by using chlorine and bromine NQR spectroscopy. The presence of bridging and terminal halogen atoms is clearly evident in BiX_4^- and $Bi_2X_9^{3-}$ salts, X = Cl, Br. Some BiX_6^{3-} salts contain discrete regular octahedral anions while others show evidence of bridging, or at least strongly associated, halogen atoms. The Raman spectra of these salts yield less decisive structural information than do the NQR spectra. General trends in ionicity as a function of the net charge on the structural unit are apparent in the NQR data now available for $BiBr_2^+$, $BiBr_3$, $BiBr_4^-$, and $BiBr_6^{3-}$ and $BiCl_3$, $BiCl_4^-$, and $BiCl_6^{3-}$. The bonding trend in $M_2X_9^{3-}$, M = Tl, Sb, Bi, is dominated by the effect of the ns^2 electron pair in the Sb and Bi.

Introduction

Bismuth(III) halide salts, through clustering of the anions, crystallize in a wide range of subtly complex structures. Salts having ion stoichiometries of $BiBr_2^+$,[1] BiX_4^-,[2,3] BiX_5^{2-},[4,5] BiX_6^{3-},[2,3] BiX_7^{4-},[2,3] $BiCl_9^{6-}$,[2] $Bi_2Br_8^{2-}$,[6] $Bi_2X_9^{3-}$,[4,7] $Bi_2X_{10}^{4-}$,[4,6] $Bi_2Cl_{11}^{5-}$,[2] $Bi_3Cl_{14}^{5-}$,[2] and $Bi_3Cl_{16}^{7-}$[8] where X = Cl^-, Br^- have been claimed, but not all have been studied with the same degree of rigor. The stoichiometry obtained appears to depend upon the cation, the concentration of the species in the crystallizing medium, and the solvent.[9] Some of the complexes may be double salts or mixtures. This occurrence has been noted in similar antimony halide systems where, for example in $Sb_2Br_{11}^{5-}$, the $Sb_2Br_9^{3-}$ ion and two Br^- ions cocrystallize in the lattice.[10]

A systematic study directed at classifying the interactions in these systems has not appeared, probably in part because

---

(1) T. Okuda, K. Yamada, H. Ishihara, and H. Negita, *Bull. Chem. Soc. Jpn.*, **50**, 3136 (1977).
(2) H. Remy and L. Pellens, *Chem. Ber.*, **61**, 862 (1928).
(3) W. Pugh, *J. Chem. Soc.*, 1385 (1954).
(4) A. Gutbier and M. Muller, *Z. Anorg. Allg. Chem.*, **128**, 137 (1923).
(5) R. L. Datta and J. N. Sen, *J. Am. Chem. Soc.*, **39**, 750 (1917).
(6) J. V. Dubsky, E. Wagonhofer, and A. Langer, *Collect. Czech. Chem. Commun.*, **11**, 441 (1939).
(7) S. M. Jorgensen, *J. Prakt. Chem.*, **3**, 328 (1871).
(8) V. Plyushehev, E. Stepina, and I. V. Vlasova, *Dokl. Akad. Nauk SSSR*, **180**, 126 (1968).
(9) R. D. Whealy and J. F. Osborne, *Inorg. Chim. Acta*, **4**, 420 (1970).
(10) S. K. Porter and R. A. Jacobsen, *J. Chem. Soc. A*, 1359 (1970).

0020-1669/80/1319-0744$01.00/0

Table I. Syntheses and Analytical Data for Chloro- and Bromobismuthate(III) Complexes

compd	method of prepn	cation to BiX_3 ratio	crystal growth medium	% calcd			% found		
				C	H	X	C	H	X
$[(C_2H_5)_2NH_2]BiCl_4$	A	1:2	*a*	11.31	2.85	33.37	11.07	2.77	33.27
$(C_2H_5NH_3)BiCl_4$	A	1:2	*a*	6.05	2.03	35.73	5.27	1.77	35.51
$(C_2H_5NH_3)_3BiCl_6$	A	3:1	*a*	13.48	4.28	37.72	13.55	4.48	38.01
$[(C_2H_5)_2NH_2]_3BiCl_6$	B	3:1	*b*	22.38	5.63	33.02	22.96	5.64	32.62
$(CH_3NH_3)_3Bi_2Cl_9$	A	1:1	*a*	4.31	2.17	38.20	4.48	2.04	38.03
$[(CH_3)_4N]_3Bi_2Cl_9$	A	1:1	*a*	15.02	3.78	33.25	14.91	3.82	33.21
$(C_5H_5NH)_3Bi_2Cl_9$	B	1:1	*d*	18.43	1.85	32.64	18.54	1.66	32.53
$(C_5H_5NH)BiBr_4$	B	1:1	*e*	9.87	0.99	52.51	10.17	1.04	52.00
$[(C_2H_5)_2NH_2]_3BiBr_6$	B	3:1	*b*	15.82	3.98	52.70	16.00	4.06	52.12
$(CH_2CHCH_2NH_3)_3BiBr_6$	B	3:1	*c*	12.52	2.80	55.51	12.97	2.81	55.35
$[(CH_3)_4N]_3Bi_2Br_9$	A	1:1	*a*	10.60	2.67	52.90	10.73	2.44	
$(CH_3NH_3)_3Bi_2Br_9$	A	1:1	*a*	2.92	1.47	58.31	3.02	1.50	58.03

[a] Growth medium was the solution used in the synthesis. [b] 48% acetone–48% 2-propanol–4% HX by volume. [c] 48% acetone–48% H_2O–4% HBr. [d] 6 M HCl. [e] 95% acetone–5% HBr.

a great deal of ion association exists in the lattice, and this fact complicates most spectral analyses. Vibrational spectroscopy of some of these compounds has been the focus of several papers.[11-15] However, as might be anticipated, agreement is not complete on the interpretation of the spectra.[13,14] All in all, the vibrational spectra do not offer a sound basis for distinguishing the various structural geometries in these salts. Most of the stoichiometries differ rather little in terms of the skeletal structure. The difference is mainly in the number of bridging vs. terminal halogen atoms and the Bi–X bond distances. Solution measurements offer little hope for establishing stoichiometry and structure in the solid state because dissociation readily occurs.[9,14,16,17] X-ray crystallography has verified the structures of salts of BiX_4^-,[18,19] BiX_5^{2-}, BiX_6^{3-},[22-24] $Bi_2Cl_8^{2-}$,[20] $Bi_2Br_9^{3-}$,[25] $Bi_2Br_{10}^{4-}$,[26] and $Bi_4Cl_{18}^{6-}$[27] where X = Cl^-, Br^-. These structures reveal the general desire of the bismuth(III) atom to attain six-coordination, either by association between ions or by stereochemical activity of the $6s^2$ electron pair.

The purpose of this paper is to report the results of a nuclear quadrupole resonance study directed at structurally classifying a series of chloro- and bromobismuthate(III) complexes. NQR spectroscopy is a powerful technique when it is used to distinguish bridging from terminal halogen atoms such as exist in these bismuth halide clusters. At the same time, some information about metal–ligand bond covalency can be extracted from the data. These systems follow our interest in obtaining electron density distribution patterns in complexes containing more than one type of NQR-active nucleus.[28,29] Both the halogen atoms and ^{209}Bi can be studied. Unfortunately, few ^{209}Bi signals were found, and the conclusions must be based primarily on halogen NQR data. Raman spectra of the salts were determined in a supportive role. However, they tend to show the futility of using vibrational data to structurally classify bismuth halide clusters in the solid state, as much as they aid in the analysis.

Experimental Section

Materials. Reagents used in the synthesis of the chloro- and bromobismuthate(III) salts were used as supplied without further purification. In the case of a number of the amines, the hydrochloride or hydrobromide salt was prepared by neutralization of the amine in cold aqueous solution by HCl or HBr.

Synthesis. Because NQR spectra are frequently obtained only on samples having good crystallinity, all of the compounds prepared for this study were crystallized by slow evaporation from either the mother liquor or another solvent as indicated in Table I.

The colorless alkylammonium chlorobismuthate(III) salts were prepared by the following methods. (A) The amine hydrochloride was dissolved in a minimum amount of H_2O and added slowly to a solution of $BiCl_3$ dissolved in a minimum amount of 6 M HCl. The mole ratios used are shown in Table I. Additional 6 M HCl was added to the solution in cases where a precipitate formed immediately. (B)[30] Bi_2O_3 was dissolved in hot concentrated HCl. A stoichiometric amount of the amine was added dropwise to this solution. The precipitate which occurred was filtered and dissolved in the growth medium indicated in Table I. If no precipitate occurred, then 6 M HCl was added, and the solution was allowed to slowly evaporate. Method A was used when amine hydrochlorides were employed in the synthesis. Method B was used when the amine alone was used.

The yellow alkylammonium bromobismuthate(III) salts were prepared similarly. One liter of a stock solution of 0.5 M $BiBr_3$ was prepared by dissolving 233 g of Bi_2O_3 in 800 mL of concentrated HBr and diluting this to 1 L with distilled H_2O. (A) The amine hydrobromide salt dissolved in a minimum amount of H_2O was added slowly to an aliquot of the 0.5 M $BiBr_3$ solution in the ratio indicated in Table I. (B)[30] Bi_2O_3 was dissolved in 20 mL of hot concentrated HBr and the amine added dropwise in the mole ratios indicated in Table I. The resulting precipitate was filtered and recrystallized from a solution of 100 mL of 2-propanol, 100 mL of acetone, and 10 mL of concentrated HBr. Crystals were then grown from the growth media listed in Table I. The ferricenium salts were prepared and verified by methods described previously.[18]

It is noteworthy that certain cations produced a particular anion stoichiometry in a rather broad range of amine-to-BiX_3 ratios. For example, $(C_2H_5)_2NH_2^+$ produces the BiX_6^{3-} salt, X = Cl, Br, in amine-to-BiX_3 ratios we tested from 2:1 to 6:1. The $BiCl_4^-$ salt forms with $C_2H_5NH_3^+$ in a 1:2 amine-to-$BiCl_3$ ratio but the $BiCl_6^{3-}$ salt in a 3:1 ratio. These aspects of bismuth halide salts were not investigated further.

Analyses. Carbon and hydrogen analyses were performed by Microanalysis, Inc., Wilmington, DE. Bromine and chlorine analyses

---

(11) R. P. Ortel and R. A. Plane, *Inorg. Chem.*, **6**, 1960 (1967).
(12) R. A. Walton, *Spectrochim. Acta, Part A*, **24**, 1527 (1968).
(13) G. Y. Ahlijah and M. Goldstein, *J. Chem. Soc. A*, 326 (1970).
(14) R. A. Work and M. L. Good, *Spectrochim. Acta, Part A*, **29**, 1547 (1973).
(15) M. A. Hooper and D. W. James, *Aust. J. Chem.*, **26**, 1401 (1973).
(16) R. A. Walton, R. W. Mathews, and C. K. Jørgensen, *Inorg. Chim. Acta*, **1**, 355 (1967).
(17) G. P. Haight, Jr., C. H. Springer, and O. J. Heilmann, *Inorg. Chem.*, **3**, 195 (1964).
(18) N. J. Mammano, A. Zalkin, A. Landers, and A. L. Rheingold, *Inorg. Chem.*, **16**, 297 (1977).
(19) B. K. Robertson, W. G. McPherson, and E. H. Meyers, *J. Phys. Chem.*, **71**, 3531 (1967).
(20) A. Hershaft and J. D. Corbett, *Inorg. Chem.*, **2**, 979 (1963).
(21) W. G. McPherson and E. A. Meyers, *J. Phys. Chem.*, **72**, 532 (1968).
(22) W. G. McPherson and E. A. Meyers, *J. Phys. Chem.*, **72**, 3117 (1968).
(23) M. Atoji and J. Watanabe, *J. Chem. Phys.*, **20**, 1045 (1952).
(24) L. R. Morss and W. R. Robinson, *Acta Crystallogr., Sect. B*, **28**, 653 (1972).
(25) F. Lazarini, *Acta Crystallogr., Sect. B*, **33**, 2686 (1977).
(26) F. Lazarini, *Acta Crystallogr., Sect. B*, **33**, 1954 (1977).
(27) B. Aurivillius and C. Stalhandske, *Acta Chem. Scand., Ser. A*, **32**, 714 (1978).
(28) D. C. Miller and T. B. Brill, *Inorg. Chem.*, **16**, 1689 (1977).
(29) T. B. Brill and D. C. Miller, *Inorg. Chem.*, **15**, 2553 (1976).

(30) T. B. Brill and G. G. Long, *J. Phys. Chem.*, **75**, 1989 (1971).

were done potentiometrically by using silver nitrate as the standard. Samples were routinely dissolved in 100–200 mL of 5–10% by volume HNO_3. A silver wire was used as the indicator electrode. The potentials were recorded against a standard calomel electrode, and electrolytic contact was made between the solutions via a KNO_3 salt bridge. No halogen analysis was obtained on $[(CH_3)_4N]_3Bi_2Br_9$ due to the insolubility of this sample in HNO_3.

NQR Spectra. The nuclear quadrupole resonance spectra were recorded on 1–3 g of polycrystalline material in tightly sealed vials. The spectra were recorded at 300 K on a superregenerative spectrometer facility which has been described before.[30] Frequency measurements are accurate to at least four significant figures below 100 MHz and five significant figures above 100 MHz. Difficulty in ascertaining the true center line of the resonance multiplet is the principal source of error in the frequency measurement.

The spectrum of each bismuth chloride sample was run in the 5-35-MHz range and that of each bismuth bromide complex in the 12–170-MHz range to ensure that no resonances would be overlooked. Resonances were not observed in about 60% of the salts we studied. Synthetic and analytical data are not included for samples which failed to yield an NQR spectrum.

Vibrational Spectra. The vibrational spectra were recorded on a Spex Model 1401 double-monochromator spectrometer employing photon counting and a spectral slit width of 150 μm. The 488.0-nm line of an argon ion laser operating at 0.4 W was used for excitation. The spectral data for each compound were collected in five scans and nine point smoothed by using a Nicolet 1180 data acquisition system. We estimate the frequencies to be accurate to ± 2 cm^{-1}. The bismuth halides are very strong light scatterers and required minimum spectrometer sensitivity. The yellow color of the bismuth bromide compounds did not hinder the spectra.

NQR Analysis

The coupling between the nuclear quadrupole moment, Q, and the largest component of the electric field gradient tensor, q_{zz}, is measured in NQR spectroscopy.[31] A coupling constant, e^2Qq_{zz}/h, in MHz can be calculated, provided the asymmetry parameter of the electric field gradient tensor, $\eta = (q_{xx} - q_{yy})/q_{zz}$, can be determined. Chlorine and bromine have $I = {}^3/_2$, so that both η and e^2Qq_{zz}/h cannot be determined directly from the spectrum of a powder sample by using conventional spectroscopy. $I = {}^9/_2$ for bismuth and this permits a unique calculation of η and e^2Qq_{zz}/h if three or more signals can be observed for each type of bismuth atom in the crystal lattice.

The resonance frequency for a chlorine or bromine nucleus depends upon both η and e^2Qq_{zz}/h according to eq 1. The

$$h\nu = e^2Qq_{zz}(1 + \eta^2/3)^{1/2}/2 \tag{1}$$

value of the frequency ν closely follows the coupling constant for values of η in the 0.0–0.5 range. Above $\eta = 0.5$, the resonance frequency may deviate from $e^2Qq_{zz}/2h$ up to 16% at $\eta = 1.0$. Halogen resonance frequencies can be used to make an accurate estimate of the field gradient only when η is small, but general trends in resonance data where the frequency differences are large still can be discussed with assurance.

The terminal halogen atoms in a bismuth halide complex have approximately axial symmetry ($\eta \leq 0.2$). Hence the resonance frequency closely follows the relationship $|N_{p_z} - N_{p_x} + N_{p_y})/2|$. N_{p_i} represents the orbital population of the ith valence p orbitals of the halogen atoms. The p_z orbital is assumed to form the Bi–X σ bond. This relationship does not include perturbations on the halogen atom by neighboring species in the crystal lattice.

The bridging halogen atoms cannot have axial symmetry. Their electric field gradient depends on the extent of σ-bond interaction between the halogen atom and the metal centers and on the Bi–X–Bi bridge angle. For angles in the 70–110° region the z principal axis of the halogen EFG tensor is perpendicular to the plane formed by the Bi–X–Bi unit. Nevertheless, in practice, NQR spectroscopy has been used very successfully to distinguish bridging from terminal halogen atoms in metal halide complexes.[29,32-34] For main-group element systems, the bridging-halogen resonance frequencies are lower than terminal-halogen frequencies,[29,32,33] while, owing to π bonding, the reverse is true in metals of the early transition series.[34] The bismuth halides cluster by bridging halogen atoms but some halogen atoms remain terminal.

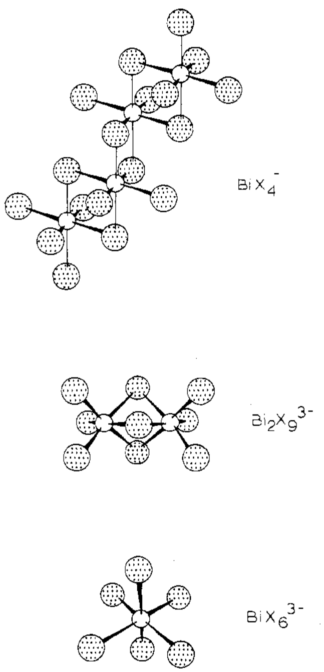


Figure 1. The structures of BiX_4^-, $Bi_2X_9^{3-}$, and BiX_6^{3-} anions, X = Cl, Br.

Structural Analyses

As noted, the structures of several bismuth(III) halide complexes have been characterized by X-ray crystallography. Figure 1 shows the geometric arrangement of the atoms in salts of BiX_4^-, BiX_6^{3-}, and $Bi_2Br_9^{3-}$ ions. The coordination sphere of the metal is dominated by the desire of bismuth(III) cation to attain six-coordination. This is accomplished by bridging corners, edges, and faces of two or more distorted octahedra. The $6s^2$ lone pair of electrons has been found to occupy a coordination position in some bismuth(III) chloride complexes[20] but it does not do so in the bismuth(III) bromides. However, the $BiBr_4^-$ chain is distorted in such a way that the bridging-halogen bond lengths are not all equivalent.[19] This fact has led to some disagreement in the interpretation of the structures.[13,14,19] In general it can be said that a great deal of association between ions is characteristic of bismuth(III) halide salts.

The difficulty of using vibrational spectroscopy to classify structural types is illustrated in Figure 2 where the Raman spectra of $(CH_3NH_3)_3Bi_2Br_9$, $[(C_2H_5)_2NH_2]_3BiBr_6$, and $(C_5H_5NH)BiBr_4$ are shown in the Bi–Br motion region. The cation modes have very little vibrational intensity in this region compared to the motions of the much more strongly polarizable Bi–Br bonds. Except for some frequency differences, the spectra of these three stoichiometries are very similar in appearance. The number of bands and their relative intensities

---

(31) T. P. Das and E. L. Hahn, *Solid State Phys., Suppl.*, **1**, Chapter 1 (1958).

(32) J. C. Evans and Y. S. Lo, *Inorg. Chem.*, **6**, 836 (1967).

(33) L. Ramakrishnan, S. Soundararajan, V. S. S. Sastry, and J. Ramakrishna, *Coord. Chem. Rev.*, **22**, 123 (1977), and references therein.

(34) D. J. Merryman, P. A. Edwards, J. D. Corbett, and R. E. McCarley, *Inorg. Chem.*, **13**, 1471 (1974).

Table II. Halogen NQR Frequencies in MHz at 300 K for Chloro- and Bromobismuthate(III) Complexes^{a}

compd	^{81}Br	^{79}Br	^{35}Cl	^{37}Cl	^{209}Bi^{b}
$[(C_2H_5)_2NH_2]_3BiX_6$	87.814 (50)	105.15 (40)	12.601 (10)	9.927 (3)	
$(C_2H_5NH_3)_3BiX_6$			10.064 (3)		
			9.295 (3)		
$(C_3H_5NH_3)_3BiX_6$^{c}	45.146 (3)	54.080 (4)			
	45.454 (3)	54.445 (4)			
	67.261 (4)	80.512 (6)			
	68.856 (5)	82.421 (8)			
$(CH_3NH_3)_3Bi_2X_9$	65.139 (20)^{b}	77.945 (20)^{b}	9.200 (4)^{b}		13.44 (3)
	92.519 (40)^{t}	110.73 (40)^{t}	12.653 (12)^{t}	9.972 (3)^{t}	14.08 (3)
			12.710 (12)^{t}	10.033 (3)^{t}	18.773 (6)
$[(CH_3)_4N]_3Bi_2X_9$	41.42 (2)^{b}	49.50 (2)^{b}			
	91.75 (3)^{t}	109.82 (3)^{t}	12.842 (3)^{t}		
$(C_5H_5NH)_3Bi_2X_9$			10.86 (2)^{b}		
			10.89 (3)^{b}		
			13.183 (6)^{t}	10.388 (2)^{t}	
			13.303 (6)^{t}	10.483 (2)^{t}	
$(C_5H_5NH)BiX_4$	53.16 (4)^{b}	63.62 (3)^{b}			
	103.67 (8)^{t}	124.05 (4)^{t}			
$[(C_5H_5)_2Fe]BiX_4$	97.447 (4)^{t}	116.59 (3)^{t}	14.739 (3)^{t}		19.664 (4)
	101.09 (4)^{t}	121.04 (3)^{t}			
	103.18 (6)^{t}	123.48 (3)^{t}			
	104.55 (4)^{t}	125.25 (3)^{t}			
$[(C_2H_5)_2NH_2]BiX_4$			13.485 (3)^{t}		
			15.425 (3)^{t}		
$(C_2H_5NH_3)BiX_4$					19.183 (3)
					22.044 (2)
					30.24 (4)

^{a} Parenthetical numbers are signal-to-noise ratios. Superscripts: b, bridge; t, terminal. ^{b} Observed in chloro salts. ^{c} $CH_2CHCH_2NH_3^+$.

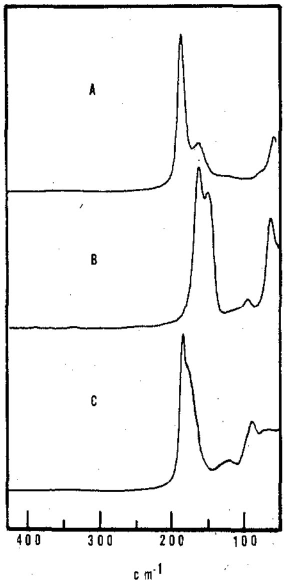


Figure 2. Raman spectra of $(CH_3NH_3)_3Bi_2Br_9$ (A), $[(C_2H_5)_2NH_2]_3BiBr_6$ (B), and $(C_5H_5NH)BiBr_4$ (C) in the Bi–Br motion region.

are comparable to the point of making distinctions between these salts quite tenuous. The similarity in the spectra is no doubt a result of the fact that in each case the coordination sphere of Bi(III) atoms differs more in the bond lengths than in the geometry.

The halogen NQR data obtained after examining a large number of chloro- and bromobismuthate(III) complexes are given in Table II. Resonances were observed in BiX_4^-, BiX_6^{3-}, and $Bi_2X_9^{3-}$ salts where X = Cl or Br. The bromine resonance assignments were verified in all compounds by the observation of resonances from both ^{79}Br and ^{81}Br in a frequency ratio of 1.197. In several instances both the ^{35}Cl (75% abundant) and ^{37}Cl (25% abundant) signals were observed in a frequency ratio of 1.269; however, these signals were generally weak, and frequently only the ^{35}Cl signal could be detected. Difficulty can arise in the chlorobismuthate(III) salts if unassignable ^{209}Bi resonances also appear. Except when the bismuth resonances can be assigned with the eigenvalue equation for $I = {}^{9}/_{2}$,[31] there is no way to distinguish ^{209}Bi signals from ^{35}Cl signals. Fortunately assignments proved to be internally reasonable.

BiX_6^{3-} Salts. According to crystal structures of one $BiBr_6^{3-}$ salt[22] and the two $BiCl_6^{3-}$ salts,[23,24] this stoichiometry contains discrete regular octahedra of MX_6^{3-} ions. The Bi–Cl and Bi–Br bond lengths from the single-crystal determinations[22,24] average 2.66 (2.52 from powder diffraction)[23] and 2.84 Å, respectively. In agreement with the regular octahedral structures, a single set of halogen resonances was observed in $[(C_2H_5)_2NH_2]_3BiX_6$, X = Cl, Br. Very closely spaced resonances produced by crystallographically inequivalent halogen atoms cannot be distinguished by using our spectrometer, but this is not important to the conclusions drawn here. The assignment of the resonances is made confident by the observation of the ^{35}Cl and ^{37}Cl pair and the ^{79}Br and ^{81}Br pair. Moreover, the ratio of $\nu_{^{81}Br}/\nu_{^{35}Cl}$ is 6.97, which is close to the value of 6.85 found in salts of octahedral MX_6^{2-} ions.[35] These results establish the anion geometry to be a regular octahedron containing only terminal halogen atoms.

Two other complexes for which the analytical data indicate the BiX_6^{3-} stoichiometry do not appear to contain unassociated regular BiX_6^{3-} octahedra. These are $(C_2H_5NH_3)_3BiCl_6$ and $(CH_2CHCH_2NH_3)_3BiBr_6$. Both yield resonance frequencies which are considerably lower than those of the other BiX_6^{3-} salts. The difference in frequency is far too large to be attributed to a counterion effect. In fact the resonance frequencies are in the range of bridging or at least highly associated halogen atoms. This is particularly true of the allylammonium hexabromobismuthate(III) salt. In accordance, the Raman spectrum of this complex reveals that the highest frequency and most intense Bi–Br vibrational mode lies at 158 cm^{-1} which is about 20 cm^{-1} less than the value of that mode in other "normal" $BiBr_6^{3-}$ salts. The allyl group has remained

---

(35) T. L. Brown and L. G. Kent, *J. Phys. Chem.*, **74**, 3572 (1970).
(36) T. B. Brill, R. C. Gearhart, and W. A. Welsh, *J. Magn. Reson.*, **13**, 27 (1974).

intact and has not become covalently associated with the anion as evidenced by the ^{13}C NMR spectrum in D_2O solution. The chemical ionization and electron-impact mass spectra also show fragmentation patterns which are expected of an unaltered allylammonium ion. A crystal structure determination of $(C_3H_5NH_3)_3BiBr_6$ will be needed to establish the anion structure with certainty.

In general, the stoichiometry of the bismuth halide cluster is not necessarily a reliable indication of the structure of the anions on the basis of the results for the BiX_6^{3-} stoichiometry. The NQR spectra reveal a notable departure from the suggested regular octahedral structure in several instances. In the others, strong evidence for a discrete octahedral BiX_6^{3-} anion is obtained.

$Bi_2X_9^{3-}$ Salts. The $[(C_6H_5)_4P]_3Bi_2Br_9$ salt contains an anion based on two octahedra sharing a face.[25] There are six terminal-bromine atoms having Bi–Br bond lengths in the range of 2.71–2.77 Å and three bridging-halogen atoms with Bi–Br bond lengths in the 2.99–3.11 Å region. The NQR spectrum of this structural unit should contain two sets of resonances corresponding to the bridging- and terminal-halogen atoms. $(CH_3NH_3)_3Bi_2X_9$, X = Cl, Br, has this spectrum. The highest frequency resonances were assigned to the terminal halogen atoms in each case. These signals were determined to be halogen resonances by the observation of resonances from the isotope pairs. The resonance pair observed at substantially lower frequency in each of these salts results from the bridging halogen atoms. A $\nu_{^{81}Br}/\nu_{^{35}Cl}$ ratio of 7.30 and 7.08 is observed for the terminal and bridging halogen atoms in $(CH_3NH_3)_3Bi_2X_9$, respectively. The intensity ratio of the terminal-to-bridging-halogen resonances is approximately 2:1 in accordance with the face-sharing octahedral structure. Similar conclusions can be drawn from $[(CH_3)_4N]_3Bi_2Br_9$ and $(C_5H_5NH)_3Bi_2Cl_9$. The terminal-halogen resonances in $[(CH_3)_4N]_3Bi_2X_9$ are very close to those in the $CH_3NH_3^+$ salt, but the bridging-bromine resonances are quite different. It is noteworthy that a recent crystal structure[27] on $(C_5H_5NH)_3Bi_2Cl_9$ reveals that the molecular formula is in fact $(C_5H_5NH)_6Bi_4Cl_{18}$. The ratio of terminal to bridging halogen atoms in this salt is still 2:1 but now two sets of bridging halogens are present. It is possible, in light of the rather low intensity of signals observed in several of these compounds, that additional bridging interactions exist, leading to higher degrees of clustering in some of these salts. We may be detecting some but not all of the bridging-halogen interactions.

Other metal halide complexes having the stoichiometry of $M_2X_9^{3-}$ follow the general NQR frequency pattern of the $Bi_2X_9^{3-}$ system. $(CH_3NH_3)_3Sb_2Br_9$ has ^{81}Br resonances at 64.78, 101.5, and 101.8 MHz.[37] Similarly, the $Tl_2Cl_9^{3-}$ ion has ^{35}Cl signals at 8.28 and 17.21 MHz.[38]

Several higher frequency resonances which we believe are ^{209}Bi signals are observed in $(CH_3NH_3)_3Bi_2Cl_9$. Unfortunately, the data are too imcomplete to permit a consistent assignment of these signals to specific transitions of ^{209}Bi. The signals in fact arise from two crystallographically different bismuth atoms. The low frequency of these resonances is consistent with the fact that the bismuth(III) atom resides in a distorted octahedral site.

BiX_4^- Salts. $BiCl_4^-$ and $BiBr_4^-$ complexes contain an infinite chain of edge-sharing BiX_6 clusters according to the crystal structures available.[18,19] The chains are helical and accommodate the cations in spaces between the chains. Each six-coordinate unit of BiX_4^- has two sets of bridging halogens and one set of terminal halogen atoms. The bond lengths of the bridging halogens are not equivalent, and this fact has led to differing interpretations of the coordinate geometry. The Bi–X bond length pairs are 2.50–2.52, 2.70–2.75, and 2.95–3.10 Å in $[(C_5H_5)_2Fe]BiCl_4$ and 2.63–2.65, 2.83–2.97, and 3.08–3.27 Å in $(2\text{-}CH_3C_5H_4NH)BiBr_4$. Not surprisingly in light of the structure, the NQR spectra of the BiX_4^- stoichiometry proved to be complex. Resonances for both bridging and terminal halogen atoms appear in some cases, but in others the spectrum is probably not complete.

A distinct set of resonances corresponding to bridging and terminal halogen atoms is observed in $(C_5H_5NH)BiBr_4$. The resonances assigned to the terminal halogen atoms are close to the values found for terminal-halogen signals in the Bi–X bonds discussed above. Similarly, the $[(C_5H_5)_2Fe]BiX_4$ salts (X = Cl, Br) and $[(C_2H_5)_2NH_2]BiCl_4$ contain resonances in the 97–104 MHz region assignable to ^{81}Br and the 13.5–15.4 MHz range due to ^{35}Cl. These also most likely arise from terminal halogen atoms, and as a group they are internally consistent in terms of the $^{81}Br/^{35}Cl$ frequency ratio of about 7. The $[(C_5H_5)_2Fe]BiBr_4$ salt would appear to contain crystallographically inequivalent $BiBr_4$ units such that more than two types of terminal halogen atoms are present.

The two types of bridging halogen atoms observed in the salts for which X-ray data are available should produce two sets of low-frequency signals. Only one of these frequency sets could be detected in $(C_5H_5NH)BiBr_4$. Careful scrutiny of the spectral recording, both with and without sample present, through the lower and higher frequency region failed to reveal any evidence of other signals.

Weak resonances are found at higher frequency in the $(C_5H_5)_2Fe^+$ and $C_2H_5NH_3^+$ salts of $BiCl_4^-$. These were tentatively assigned to ^{209}Bi signals, but it is necessary to consider whether or not they can be reasonably assigned to the terminal ^{35}Cl resonances. We are confident that they cannot be. First of all, the ^{35}Cl signals in $BiCl_3$ have been observed at 15.955 and 19.155 MHz.[39] The ^{35}Cl signals in $BiCl_4^-$ might be expected to lie somewhat lower in frequency than these signals because of the increased ionicity present in the $BiCl_4^-$ unit compared to $BiCl_3$. Secondly, if these resonances belong to terminal chlorine atoms, the $^{81}Br/^{35}Cl$ frequency ratio of about 7 would call for ^{81}Br signals above 134 MHz in the corresponding $BiBr_4^-$ salts. In no instance was any signal found higher than 104.5 MHz that could be assigned to ^{81}Br in $BiBr_4^-$. This frequency range even far exceeds the ^{81}Br resonances observed in $BiBr_3$.[40] Thus, it seems unlikely that the resonances above 19 MHz in $BiCl_4^-$ salts belong to ^{35}Cl, and they must be ^{209}Bi resonances.

Electronic Effects

Because of the high degree of interionic association that exists in these halobismuthate(III) complexes, only qualitative conclusions about the nature of bonding will be drawn.

The effect of increasing the number of halogen atoms around the bismuth(III) ion is evident in the trend of ionicity of the terminal Bi–Br bond. In the series $BiBr_2^+$, $BiBr_3$, $BiBr_4^-$, and $BiBr_6^{3-}$ the ^{81}Br resonance frequency of the terminal halogen atoms follows the trend 148,[1] 110,[35] 101, and 88 MHz. This decrease in frequency reflects the increase in the Bi–Br bond ionicity with increasing negative charge on the complex. The increase in ionicity results from a buildup of electron density in the metal–halogen σ-bond orbital. The bond lengths of the terminal bismuth–bromine bonds in $BiBr_4^-$ (2.66 Å), $Bi_2Br_9^{3-}$ (2.74 Å), and $BiBr_6^{3-}$ (2.84 Å) crudely follow the bromine atom resonance frequency (101, 92, and 88 MHz). The trend is perhaps fortuitous in light of the fact that NQR frequencies and bond-length data do not correlate in all cases.[36]

---

(37) T. B. Brill, P. E. Garrou, and G. G. Long, *J. Inorg. Nucl. Chem.*, **33**, 3285 (1971).

(38) D. E. Scaife, *Aust. J. Chem.*, **23**, 2205 (1970).

(39) H. G. Robinson, *Phys. Rev.*, **100**, 1731 (1955).

(40) Y. Furukawa, *J. Sci. Hiroshima Univ., Ser. A: Phys. Chem.*, **37**, 357 (1973).

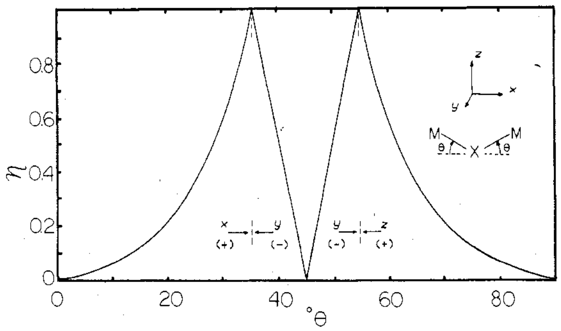


Figure 3. A point-charge model calculation of the asymmetry parameter of X as a function of nonlinearity of the MXM unit as shown. The principal axis of the electric field gradient is also indicated as a function of the angle (*y* is perpendicular to the MXM unit).

A less clear correlation exists in the bismuth chloride series. The Bi–Cl bond lengths are 2.47–2.52, 2.50–2.52, and 2.52[23] or 2.66 Å[24] in $BiCl_3$, $BiCl_4^-$, and $BiCl_6^{3-}$, respectively, and the ^{35}Cl resonance frequencies for terminal linkages in this series fall in the ranges of 19.1–15.4, 15.4–13.5, and 13.3–12.6 MHz.

The electronic structure of the bridging halogen atoms is difficult to establish because of their nonaxially symmetric electric field gradient tensor. The ratio of the resonance frequency for terminal to bridging halogen atoms covers a broad range in these compounds. The difference in Bi–Br–Bi angles ranging from 90–97° in $BiBr_4^-$ [19] to 82–85° in $Bi_2Br_9^{3-}$ [25] contributes to some of this variation, particularly as the angle approaches 70 or 110°. Figure 3 is based on the point-charge model[41] and shows the effect of changes in the bridge angle on the asymmetry parameter of the bridging element. The halogen resonance frequency can change to 16% as the angle changes. Other factors, such as bond length and the number of bridging vs. terminal halogen atoms, play a role in the electric field gradient of the bridging halogen atom.

The most interesting electronic feature of the Bi(III) core is the effect of the $6s^2$ electron pair. This effect can be most directly noted when Bi(III) is compared to Sb(III) and Tl(III) in structurally similar compounds. In $M_2Br_9^{3-}$ salts, the electric field gradient of the terminal bromine atoms is greater in Sb(III)–Br bonds than in Bi(III)–Br bonds, reflecting the greater covalency of the Sb–Br bonds compared to that of Bi–Br bonds.

The presence of the $6s^2$ electron pair in Bi(III) may be used to rationalize the electric field gradient differences in $Bi_2Cl_9^{3-}$ compared to $Tl_2Cl_9^{3-}$.[38] The terminal Tl–Cl bonds appear to be much more covalent than the Bi–Cl bonds because Bi(III) experiences reduced effective nuclear charge as a result of the presence of the $6s^2$ pair.

Registry No. $[(C_2H_5)_2NH_2]BiCl_4$, 72318-13-9; $(C_2H_5NH_3)BiCl_4$, 72318-14-0; $(C_2H_5NH_3)_3BiCl_6$, 18756-47-3; $[(C_2H_5)_2NH_2]_3BiCl_6$, 72318-15-1; $(CH_3NH_3)_3Bi_2Cl_9$, 72318-16-2; $[(CH_3)_4N]_3Bi_2Cl_9$, 43093-29-4; $(C_5H_5NH)_3Bi_2Cl_9$, 72318-17-3; $(C_5H_5NH)BiBr_4$, 72318-12-8; $[(C_2H_5)_2NH_2]_3BiBr_6$, 29718-11-4; $(CH_2CHCH_2NH_3)_3BiBr_6$, 29532-28-3; $[(CH_3)_4N]_3Bi_2Br_9$, 15809-67-3; $(CH_3NH_3)_3Bi_2Br_9$, 72318-18-4; $[(C_5H_5)_2Fe]BiBr_4$, 72318-11-7; $[(C_5H_5)_2Fe]BiCl_4$, 61026-19-5.

---

[41] T. B. Brill, *J. Magn. Reson.*, **15**, 395 (1974).

Contribution from the Department of Chemistry,
University of Delaware, Newark, Delaware 19711

Electronic Structure Properties of Exo-Substituted Cyclohexadienylmanganese Complexes Based on ^{55}Mn NQR Spectroscopy

T. B. BRILL,* W. C. FULTZ, and B. R. HOFMANN

Received July 25, 1979

The series of tricarbonylcyclohexadienylmanganese(I) complexes, $C_6H_6XMn(CO)_3$, X = H^-, $CH(CO_2C_2H_5)_2^-$, and CN^-, have been examined by ^{55}Mn NQR spectroscopy. The very large value of the electric field gradient asymmetry parameter results from a difference in population of the d_{xz} and d_{yz} orbitals on manganese. The asymmetry parameter in this series of compounds is inversely proportional to the coupling constant which can only occur if the difference in the population of these two orbitals remains constant. Comparison of calculated transition probabilities to theoretical values for the $\pm^5/_2 \leftrightarrow \pm^3/_2$ and $\pm^3/_2 \leftrightarrow \pm^1/_2$ transitions of ^{55}Mn show the same trend and provide support for Cohen's tables. A forbidden transition for ^{55}Mn was observed for what we believe is the first time by using a superregenerative oscillator.

Introduction

The electronic structures of cyclohexadienyl transition-metal tricarbonyl complexes have come under scrutiny by using theoretical methods with an eye to understanding their geometric deformations,[1] reactivity,[2] NMR spectra,[3] and place in the scheme of metal-ring fluxionality.[4] Although NMR spectroscopy is useful for studying the ring,[3] experimental methods capable of probing small changes in the ground-state electronic properties of the metal in these complexes are less handy. This fact limits the availability of data with which one might explain the behavior of the complexes and analyze the theoretical conclusions. Nuclear quadrupole resonance spectroscopy is a potentially useful technique for examining small changes in the electronic structure of metals. It has been applied to an increasing extent to this role.[5]

In this project the electric field gradient properties of the metal atom in tricarbonylcyclohexadienylmanganese(I), **1**,

---

[1] R. Hoffmann and P. Hofmann, *J. Am. Chem. Soc.*, **98**, 598 (1976).

[2] D. W. Clack, M. Monshi, and C. A. P. Kane-McGuire, *J. Organomet. Chem.*, **107**, C40 (1976).

[3] P. A. Dobosh, D. G. Gresham, D. J. Kowalski, C. P. Lillya, and E. S. Magyar, *Inorg. Chem.*, **17**, 1775 (1978).

[4] T. H. Whitesides, D. L. Lichtenberger, and R. A. Budnik, *Inorg. Chem.*, **14**, 68 (1975).

[5] T. B. Brill, "Advances in Nuclear Quadrupole Resonance Spectroscopy", Vol. III, J. A. S. Smith, Ed., Heyden & Sons, London, 1978.

0020-1669/80/1319-0749$01.00/0