Crown Ether Size Effects, Effective Matrix Isolation of Metal Halide, Ligand Conformation, and Halogen Bridging in Cadmium Halide–Polyether Adducts. A Nuclear Quadrupole Resonance, Infrared, and Raman Study

By **Gary Wulfsberg** *,† and **Alarich Weiss**, Physikalische Chemie III, Technische Hochschule, Petersenstrasse 15, D-6100 Darmstadt, Germany

Adducts of composition mCdX$_2$·polyether (X = Cl, Br, or I; m = 1, 1.5, 2, or 3) have been prepared with the polyethers $CH_3O[CH_2CH_2O]_{n-1}CH_3$ (n = 2—5) and the crown ethers $\lfloor[CH_2CH_2O]_n\rfloor$ (n = 5 and 6). I.r. and Raman spectra show that the polyethers chelate in the 1 : 1 adducts, but have different conformations for $m \neq 1$. The effects of CdX$_2$ and HgX$_2$ on the different C–O stretching and C–O–C bending modes are given. Metal–halogen stretching frequencies (from the Raman spectra) and halogen n.q.r. frequencies are reported, and assigned to bridging and terminal halogens. Analysis of these frequencies as a function of the number n of oxygen atoms in the polyether allows the frequencies of matrix-isolated CdI$_2$ and HgX$_2$ to be estimated, and reveals anomalies in the n.q.r. spectra of CdX$_2$·18-crown-6. These anomalies are explained in terms of the mismatch of the radii of the metal and the 18-crown-6 cavity.

CHEMISTS have often sought to explain the many dissimilarities in the chemistry of the Group 2B metals cadmium and mercury in terms of differences in their electronic configurations or energies.[1] N.q.r. spectroscopy [2] is potentially a valuable method for studying the electronic distribution in the halides of these metals, and has often been used with derivatives of the mercury halides.[3,4] However, very little work has been done with cadmium analogues.[5-10] There is, for example, a striking anomaly in the n.q.r. frequency of CdBr$_2$ (14.318 MHz at 77 K) [6] as compared to ZnBr$_2$ (81.425—84.137 MHz) [6] or HgBr$_2$ (129.90 and 130.93 MHz); [11,12] similar results are found in the iodides.

It is known [3] that the bridging function of the halogens in the solid mercury halides substantially affects their n.q.r. frequencies. There are differences in the bridging in CdX$_2$ (octahedral co-ordination of Cd), ZnX$_2$ (probably tetrahedral co-ordination of Zn), and pseudo-molecular HgX$_2$.[13] In the study of the effects of bridging, we gradually isolated HgX$_2$ units by co-ordinating them with progressively longer chelating polyether ligands, the glymes, $CH_3O(CH_2CH_2O)_{n-1}CH_3$ (1a—d) and finally the crown ether 18-crown-6, $\lfloor[CH_2CH_2O]_6\rfloor$. Here this is done with the cadmium halides. Adducts of cadmium halides with simple ethers and dioxan,[14,15] with the polyethers glyme [16-18] and polyethylene oxide,[19] and with 18-crown-6 [20] and dibenzo-18-crown-6 [21] are known, but only one adduct of CdX$_2$ with the medium-length polyethers has been prepared.[22a] Hence the preparation and

---

† *Present address:* Department of Chemistry, St. Johns University, Collegeville, Minnesota, 56321.

[1] L. E. Orgel, *J. Chem. Soc.*, 1958, 4186.

[2] E. A. C. Lucken, 'Nuclear Quadrupole Coupling Constants,' Academic Press, New York, 1969.

[3] G. Wulfsberg, *Inorg. Chem.*, 1976, **15**, 1791, and refs. therein.

[4] W. Fichtner and A. Weiss, *Z. Naturforsch.*, 1976, **316**, 1626.

[5] R. G. Barnes, S. L. Segel, and W. H. Jones, *J. Appl. Phys.*, 1962, **33**, 296.

[6] T. J. Bastow and H. J. Whitfield, *Austral. J. Chem.*, 1974, **27**, 1397.

[7] D. L. Lyfar, V. E. Goncharuk, and S. M. Ryabchenko, *Physica Status Solidi* (*Berlin*), Part 6, 1976, **76**, 183.

[8] G. K. Semin, T. A. Babushkina, and G. G. Yakobson, 'Nuclear Quadrupole Resonance in Chemistry,' Israel Program for Scientific Translations, Jerusalem, 1975.

[9] (*a*) R. Kind, S. Plesko, and J. Roos, *Ferroelectrics*, 1976, **13**, 433; (*b*) K. S. Aleksandrov, A. K. Moskalev, V. L. Serebrennikov, V. M. Buznik, and B. V. Beznosikov, *Izvest. Akad. Nauk S.S.S.R., Ser. fiz.*, 1975, **39**, 2474.

[10] T. A. Babushkina, O. Kh. Poleshchuk, Yu. K. Maksyutin, A. M. Alymov, S. D. Sokolov, and E. I. Mikhailovskaya, *Koord. Khim.*, 1975, **1**, 1266.

[11] Yu. K. Maksyutin, E. N. Gur'yanova, and G. K. Semin, *Russ. Chem. Rev.*, 1970, **39**, 334.

[12] D. Nakamura, Y. Uehara, Y. Kurita, and M. Kubo, *J. Chem. Phys.*, 1959, **31**, 1433.

[13] A. F. Wells, 'Structural Inorganic Chemistry,' Clarendon Press, Oxford, 1975, 4th edn.

[14] J. C. Barnes and C. S. Duncan, *J. Chem. Soc.* (*A*), 1969, 1746.

[15] H. Rheinboldt, A. Luyken, and H. Schmittmann, *J. prakt. Chem.*, 1937, **149**, 30.

[16] (*a*) G. W. A. Fowles, D. A. Rice, and R. A. Walton, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3119; (*b*) G. W. A. Fowles, P. T. Greene, and T. E. Lester, *ibid.*, 1967, **29**, 2365; (*c*) G. W. A. Fowles, T. E. Lester, and J. S. Wood, *ibid.*, 1969, **31**, 657; (*d*) G. W. A. Fowles, D. A. Rice, and R. A. Walton, *Spectrochim. Acta*, 1970, **26A**, 143.

[17] W. Ludwig and H. P. Schroeer, *Z. anorg. Chem.*, 1968, **357**, 74.

[18] N. R. Chaudhuri and S. Mitra, *Bull. Chem. Soc. Japan*, 1975, **48**, 2837.

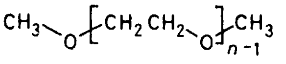
[19] A. A. Blumberg, S. S. Pollack, and C. A. J. Hoeve, *J. Polymer Sci.* (*Part A Polymer Phys.*), 1964, **2**, 2499.

[20] A. Knöchel, J. Klimes, J. Oehler, and G. Rudolph, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 787.

[21] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 7017.

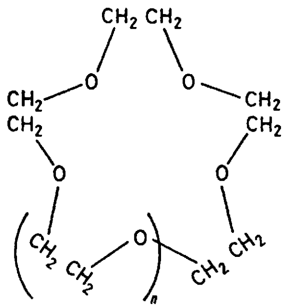
[22] (*a*) R. Iwamoto and H. Wakano, *J. Amer. Chem. Soc.*, 1976, **98**, 3764; (*b*) R. Iwamoto, 'Structural Studies of Crystalline Complexes of Poly(ethylene Oxide) and its Oligomers with Mercuric Chloride,' Government Industrial Research Institute Report No. 342, Osaka, 1972; (*c*) R. Iwamoto, *Spectrochim. Acta*, 1971, **27A**, 2385; (*d*) R. Iwamoto, *Bull. Chem. Soc. Japan*, 1973, **46**, 1114, 1118, 1123, 1127.

properties of these adducts are described in the Experimental section.



(1)

a; $n = 2$ (2,5-dioxahexane or glyme)
b; $n = 3$ (2,5,8-trioxanonane or diglyme)
c; $n = 4$ (2,5,8,11-tetraoxadodecane or triglyme)
d; $n = 5$ (2,5,8,11,14-pentaoxapentadecane or tetraglyme)



(2)

a; $n = 1$ (1,4,7,10,13-pentaoxacyclopentadecane or 15-crown-5)
b; $n = 2$ (1,4,7,10,13,16-hexaoxacyclo-octadecane or 18-crown-6)

EXPERIMENTAL

Cadmium halides ($CdCl_2{\cdot}H_2O$, $CdBr_2{\cdot}4H_2O$, and CdI_2), the polyethers, analytical grade tetrahydrofuran (thf), and ethyl orthoformate were obtained from Merck, Darmstadt; 18-crown-6 was obtained from Fluka AG. Denatured ethanol was used as a solvent; the dioxan had previously been purified and stored over sodium wire.

The glyme, thf, and dioxan adducts were prepared as previously described.[14,16] The adducts of the higher polyethers were prepared in four ways. (i) The cadmium halide was dissolved in hot ethanol, treated with triethyl orthoformate to dehydrate it, and an equimolar amount of polyether was added. (In some experiments with CdI_2 only a half-molar quantity of polyether was used, with no alteration of the results.) Usually cooling or partial evaporation was needed to produce crystals. (ii) The cadmium halide was treated with ethyl orthoformate, then refluxed with excess of polyether; the products were of low solubility even in the hot polyether. (iii) Cadmium halide and an equimolar amount of polyether were dissolved in water, and the solution allowed to evaporate. Large crystals resulted before evaporation was complete. (iv) For CdI_2·18-crown-6 and CdI_2·15-crown-5, the CdI_2 was dissolved in thf and added to commercial crown ether dissolved in diethyl ether; the adduct was precipitated. This procedure differs slightly from that used by Knöchel.[20]

Melting points were measured in sealed capillaries or on a melting-point block, but most adducts lost polyether without melting. Halogen was analysed by the Volhard method, and carbon and hydrogen were determined by combustion. In Table 1 are summarized the stoicheiometries of the adducts, their methods of preparation, qualitative solubilities, melting points, and analytical data.

I.r. spectra of samples in mineral-oil mulls were recorded over the ranges 750—1 350 and 3 000—3 600 cm^{-1} on a Beckmann IR-7 spectrometer. Raman spectra were recorded on a Coderg LRT-800 instrument with a Spectra Physics 164 laser using 5 145-Å exciting light at power levels of 0.05—0.8 W. Samples for Raman spectroscopy

TABLE 1

Analytical results, methods of preparation, and properties of polyether adducts

						Analyses (%)					
		Solubility [c]				Found			Calculated		
1 : 1 Adducts [a]	Prep.[b]	H_2O	EtOH	$CHCl_3$	M.p.[d] (θ_c/°C)	C	H	Hal	C	H	Hal
CdI_2·diglyme	1	s	s	s, decomp.	112—116 (decomp.)	14.3	2.8	50.1	14.4	2.8	50.7
CdI_2·triglyme	1,2	s	s	s, decomp.	114.5—116	17.7	3.35	46.35	17.65	3.35	46.6
CdI_2·tetraglyme	1, 2, 3	s	s	s	124 (decomp.)	20.45	3.85	43.1	20.5	3.8	43.15
$CdBr_2$·tetraglyme	2	s	decomp.	decomp.		24.3	4.6	32.05	24.3	4.5	32.3
CdI_2·18-crown-6	4	i	i	s	273—277	22.9	3.85	39.25	22.85	3.85	40.25
$CdBr_2$·18-crown-6	1	i, decomp.	i	s	276—279	26.95	4.6	29.6	26.85	4.5	29.8
$CdCl_2$·18-crown-6	1	i, decomp.	i	s	>200 (decomp.)			15.75			15.85
Other adducts											
$2CdCl_2$·diglyme·H_2O [e]	1	s	s			12.85	3.05	27.5	13.9	3.1	27.35
$2CdBr_2$·diglyme	1, 2	s	s	i		10.65	2.05	47.1	10.6	2.1	47.1
$3CdBr_2$·2diglyme·$3H_2O$ [e]	3	s	s			12.85	2.95	42.15	12.65	3.15	42.1
$2CdCl_2$·triglyme	1	s	s					26.1			26.05
α-$2CdBr_2$·triglyme	1, *f*	s	s	i		13.3	2.5	44.3	13.3	2.5	44.25
β-$2CdBr_2$·triglyme	3, *f*	s	s			13.35	2.6	43.4	13.3	2.5	44.25
$2CdCl_2$·tetraglyme	1, 2	s	i					24.15			24.1
$2CdBr_2$·tetraglyme	1, 3	s	s	i		16.05	2.95	41.5	15.65	3.05	41.7
$3CdBr_2$·15-crown-5	1	i, decomp.	i	i	279—281 (decomp.)	11.55	1.9	46.0	11.6	1.95	46.25
1.$2CdI_2$·15-crown-5	4	i, decomp.	i	i	223—227	17.45	3.25	45.65	18.2	3.05	46.15

[a] Glymes are $CH_3O[CH_2CH_2O]_{n-1}CH_3$: $n = 3$, diglyme; $n = 4$, triglyme; $n = 5$, tetraglyme. [b] Method of preparation (see Experimental section): 1 = ethanol, 2 = excess of polyether, 3 = water, 4 = thf–diethyl ether. [c] Qualitative solubility: s = soluble; i = insoluble; s, decomp. = soluble but partially decomposed; i, decomp. = insoluble at first, then dissolves (presumably *via* hydrolysis). [d] Melting point, if observed: other adducts decomposed with loss of polyether but without melting, between 100 and 200 °C. [e] Degree of hydration uncertain. Calculated for amount of water shown. [f] Mixture of α and β forms produced by method 2.

TABLE 2

Vibrational spectra of the pure crystalline polyethers, their 1 : 1 CdX_2 adducts, and their HgX_2 adducts. I.r. spectra from 1 350 to 800 cm^{-1}; Raman spectra from 800 to 280 cm^{-1}. Spectra of the pure polyethers and the CdX_2 adducts are expressed as shifts[a] of the corresponding absorption bands of the $HgCl_2$ adducts

Acyclic polyethers

Vibrational mode	Glyme[b]			Diglyme		Triglyme		Tetraglyme	
	Pure[b]	$HgCl_2$[c]	CdI_2	$HgCl_2$[c]	CdI_2	$HgCl_2$[c]	CdI_2	$HgCl_2$[c]	CdI_2
Methylene twist[d,e]								1 351m	−2
				1 345m	+4	1 341m	+2	1 342m	−3
	0	1 287m	−9	1 280m	0	1 284m	0	1 285m	−3
				1 270 (sh)	−3			1 276 (sh)	−5
	+3	1 242m	−5	1 243m	+3	1 243m	0	1 245m	−2
				1 234 (sh)	+1			1 237 (sh)	*f*
						1 227 (sh)	+1	1 228 (sh)	*f*
Methyl rock[d,e]	+7	1 201 (sh)	+3	1 199m	+4	1 191m	+5	1 196m	−3
	+9	1 193m	−2	1 191 (sh)	*f*				
	+19	1 157m	+3	1 159m	−1	1 154 (sh)	+5	1 160w	+8
	+17	1 154 (sh)	−2						
C–O stretch,	+13	1 124s	−8	1 129s	−17	1 129s	−9	1 129s	−19
methylene rock[e]	−11	1 117s	−1	1 101vs	−5	1 108 (sh)	−11	1 108vs	−16
	+9	1 019vs	+5	1 093s	−7	1 099vs	−11	1 100 (sh)	−18
	+17	1 076vs	−10	1 076vs	−10			1 089 (sh)	−20
	+13	1 064 (sh)	*f*	1 067 (sh)	−9	1 073vs	−11	1 083s	−25
								1 065m	−27
Methyl rock[d]	+10	1 027m	−3	1 029m	−3	1 029vw	+3		
	+13	1 015s	−1	1 013m	−4	1 020m	0	1 024s	−7
Chelating $C_2H_4OC_2H_4$[g]								968vw	+14m
				939m	+3	944m	+1	947s	−1
						937 (sh)	*f*	930 (sh)	−5
C–O stretch,	+9	849vs	+11	857m	+11	855m	+13	857m	+6
C–C stretch[e]						844m	+3	844m	−3
	+18	840vs	−8	839m	+1			835m	−10
				828m	−4	826m	−10	827m	−18
C–O–C, O–C–C bend[e,h]	−5	575w	0	574w	*f*	576vw	−8	576w	−14
				548w	*f*	555w	0	562w	−17
								524w	0
C–O–C bend[e,h]				388vw	*f*	362vw	*f*	378w	+2
								345w	+13
	−33	372m	+9	342m	+9	313m[i]	+12	295s	+25
	+8	300vw	0	305w	*f*				

Cyclic polyethers

Vibrational mode	1-4-dioxan, i.r.			18-crown-6, i.r.			18-crown-6, Raman			15-crown-5
	Pure	$HgBr_2$[j]	$CdBr_2$	$HgCl_2$	$CdBr_2$	KBr[k]	$2CH_3CN$[l]	$HgCl_2$	$CdBr_2$	$3CdBr_2$
Methylene twist[d,e]				1 346s	+2	+2, −6				1 345m
	+8	1 288s	−4	1 283m	−3	+3, −8				1 283vw
							+6	1 273m	−2	1 270m
	+5, 12	1 253s	+3	1 263vw	−6	−8				1 257vw
				1 245m	−6	−1	+7	1 243w	−2	1 246m
				1 231m	−14	−1				1 236m
				1 208vw	−4	*f*				
							+6	1 144w	0	1 130w
C–O stretch,	+2	1 127 (sh)	−17	1 136m	−6	*f*	+5	1 138w	−1	1 107m
methylene rock[e]	+4	1 113vs	−11	1 110vs	−3	−7	+4	1 107vw	+6	1 089 (sh)
	+8	1 080m	−10				0	1 085w	+2	1 074vs
							+10	1 063vw	+3	1 041m
				1 054m	−1	−1				1 031m
	+14	1 038m	−5							1 020m
Chelate[g]				961vs	+8	−1	−2	950w	+10	943s
C–O stretch,	+5	889s	−9				−3	868m	+11	855vw
C–C stretch[e]	+15	856vs	−6	838vs	+5	+2				826m
				(838)	−3	−6	0	837w	−2	819m
										813m
										785w
C–O–C,	−2	488vw	0				+5	548m	+3	540m
O–C–C										515w
bend[e,h]	−4	426vw	−4				+1	368w	+3	
	−19	451m	+20				+7	280m[i]	+8	349s

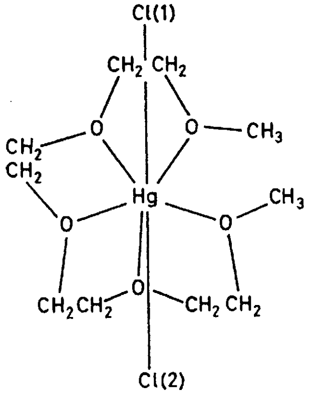
[a] Shifts are listed as cm^{-1} above (+) or below (−) the wavenumbers of the absorption bands of the HgX_2 adducts. Intensities are indicated in the usual manner. Errors are estimated as ±1 cm^{-1} for the i.r. and ±3 cm^{-1} for the Raman frequencies. [b] The polyether component of the adduct is listed first, above the metal halide component, or above the word 'pure' for the spectra of the pure crystalline polyether. [c] Similar data first reported in ref. 22*b*. [d] Assigned in ref. 26 for the pure liquid glymes [e] Assigned in ref. 24 for pure crystalline 1,4-dioxan and glyme. [f] Not detected. [g] Assigned in ref. 22*b* for the mercury chloride adducts of the glymes. [h] Raman spectra. [i] In $HgBr_2$ adduct. [j] Similar data first reported in ref. 16*d*. [k] Data from R. Costes, G. Folcher, P Plurien, and P. Rigny, *Inorg. Nuclear Chem. Letters*, 1976, **11**, 13. [l] Data for acetonitrile adduct from ref. 36.

were in polycrystalline form, or were dissolved in acetone or the ligand itself.

N.q.r. spectra were measured with a Decca Radar n.q.r. spectrometer, with oscillator heads operating in the 6—90 and 100—300 MHz ranges. $CdBr_2$ adducts were searched at room temperature and 77 K, generally over the range 50—72 MHz; the ^{81}Br n.q.r. frequencies reported were confirmed by observing the ^{79}Br n.q.r. signals at the appropriate frequencies. CdI_2 adducts were searched for ^{127}I $m = \pm 1/2 \rightleftharpoons \pm 3/2$ and $m = \pm 3/2 \rightleftharpoons \pm 5/2$ transitions at room temperature over the range 100—220 MHz, and at 77 K in a range *ca.* 7 MHz above and below the room-temperature frequency. Hence, if the compound underwent a drastic structural change between these temperatures, signals would have been missed; but as the temperature variations of these frequencies were quite regular,[23] this is considered to be unlikely. For both bromide and iodide samples, the search ranges were extended as needed to include the frequencies of the corresponding adduct of the next higher and next lower polyether. Only brief efforts were made to locate ^{35}Cl signals, as these were expected (for most samples) to fall below 9 MHz, where the sensitivity is low.

RESULTS

I.r. and Raman Spectra in the Region of Ligand Absorptions.—Flexible ligands such as the polyethers can have many conformations, to which their i.r. and Raman spectra should be sensitive. Iwamoto[22b,c] studied the i.r. spectra of the $HgCl_2$ adducts of the first four glymes and found them to be quite similar. His *X*-ray study of $HgCl_2$·tetraglyme[22d] showed the ligand to have a completely chelating conformation (3). He therefore postulated chelating conformations for the $HgCl_2$ adducts of the shorter polyethers.



(3) $CN_{Hg}=7$: $CN_{Cl(1)}=CN_{Cl(2)}=1$

In Table 2 are presented our measurements of the i.r. spectra of the $HgCl_2$ adducts; these are very similar to those of Iwamoto.[22b] Below 600 cm^{-1} Raman frequencies are listed. The bands of the CdI_2 1 : 1 adducts are also listed, as apparent frequency shifts of the corresponding $HgCl_2$ bands. Because of the strong resemblances of the spectra of the 1 : 1 CdX_2 adducts to those of the HgX_2 adducts, it is postulated that the 1 : 1 CdX_2 adducts also have the chelating conformation (except for the dioxan adducts). Additional support for this conclusion comes from the resemblance of these spectra to the (incompletely reported) spectra[16b] of $[TiBr_2(glyme)_2][TiBr_4(glyme)]$, which is known by *X*-ray crystallography[16c] to have chelating ligands. These spectra also resemble that calculated and found for glyme itself in the chelating *tgt* conformation.[24] It should also be mentioned that diglyme is chelating in its adduct with $Cd[Mn(CO)_5]_2$.[25]

The compounds of other stoicheiometries have strikingly different i.r. and Raman spectra, which are listed in Table 3. It is clear that the conformations of the polyethers in these compounds must be other than totally chelating. In the case of $2CdCl_2$·tetraglyme, Iwamoto[22a] has shown by *X*-ray crystallography that the tetraglyme chelates one cadmium atom with four oxygen donor atoms, and the other cadmium with the fourth and fifth oxygen atoms. The fourth oxygen atom is bridging between the two cadmium atoms. The other spectra in Table 3 are simpler than those of $2CdX_2$·tetraglyme (X = Cl or Br), which perhaps suggests more symmetrical conformations, but it is not possible to deduce the conformations in detail. There does appear to be a tendency to a lower frequency for the most intense C–O stretching mode in the non-chelating ligands than in the chelating ligands.

The spectra of crystalline glyme and dioxan, the $HgCl_2$–polyether adducts, and the liquid higher polyethers have been assigned;[22b,24,26] these assignments are listed in Table 2. We note that the frequencies corresponding to methyl or methylene motions are little affected by formation of a CdX_2 or HgX_2 adduct, whereas those associated with C–O stretching or C–O–C bending modes show larger shifts. Most of the latter ones are shifts to lower frequencies in the series (free ligand) > (HgX_2 adduct) > (CdX_2 adduct). Such a shift of the C–O stretching frequencies of thf on forming complexes has previously been noted,[27a] and is consistent with CdI_2 having a higher Lewis acidity than $HgCl_2$. The bands at *ca.* 850 and 300 cm^{-1}, however, are shifted in the other direction. Such observations might be useful in assigning vibrational modes in these spectra. Shifts are substantially absent in the 18-crown-6 adducts, perhaps due to their rigidity.

Two bands appear characteristic of the chain length: the 940 cm^{-1} band, found only in diglyme or higher polyethers,[22b] and the 372—280 cm^{-1} band, which shifts substantially both with chain length[26] and upon adduct formation. The 982 cm^{-1} band in CdX_2·tetraglyme is much more intense (medium *vs.* very weak) than the corresponding band in HgX_2·tetraglyme, which might indicate a slight conformational change.

Raman Spectra in the Metal–Halogen Region.—In the 100—300 cm^{-1} region one intense Raman absorption band was usually found, which was assigned to the symmetric metal–halogen stretching (or for chain structures, *etc.*, a related) mode. These frequencies are tabulated in Table 4, along with frequencies of model compounds which are monomeric and which have halogen bridging. There is a reasonable resemblance between our results and those reported[27b] for MX_2 dissolved in another oxygen donor, tributylphosphate.

---

[23] G. Wulfsberg and A. Weiss, unpublished data.

[24] R. G. Snyder and G. Zerbi, *Spectrochim. Acta*, 1967, **23A**, 391.

[25] W. Clegg and P. J. Wheatley, *J.C.S. Dalton*, 1974, 424.

[26] K. Machida and T. Miyazawa, *Spectrochim. Acta*, 1964, **20**, 1865.

[27] (*a*) R. J. Kern, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1105; (*b*) D. N. Waters, E. L. Short, M. Tharwat, and D. F. C. Morris, *J. Mol. Structure*, 1973, **17**, 389.

TABLE 3

I.r. and Raman spectra of 2 : 1 and 3 : 2 adducts. I.r. spectra above 775 cm^{-1}; Raman spectra below 775 cm^{-1}

$2CdCl_2\cdot$diglyme$\cdot H_2O$	$3CdBr_2\cdot$2-diglyme$\cdot 3H_2O$	$2CdBr_2\cdot$diglyme	α-$2CdX_2\cdot$triglyme ^{a}	β-$2CdBr_2\cdot$triglyme	$2CdX_2\cdot$tetraglyme ^{a}
1 352m	1 311w	1 349w			1 352m, 1 340m
1 307w	1 294m	1 312m	1 303m	1 298w	1 316m
1 282m	1 284w	1 276m	1 269m		1 280m, 1 264w
1 254m	1 255m			1 256vw	1 258w
1 240m	1 239m	1 247m	1 246m	1 246m	1 243s
1 201s	1 200m	1 198m	1 193m	1 197w	1 205w, 1 198m
1 141s	1 135m	1 126vw			1 128m
1 109s	1 119m		1 115m	1 109m	1 111s, 1 106s
	1 092 (sh)	1 1087s	1 092s	1 097s	1 099s, 1 091s
1 086vs	1 087vs	1 080s			1 076vs
1 065 (sh)	1 054vs		1 054vs	1 060vs	1 052s
	1 028s	1 027vs	1 048 (sh)		1 037s
1 023s	1 017s	1 011m	1 026s	1 028m	1 022s
			1 020m	1 011m	1 008s
980m	998m	999s	990m		
946m	978w		977vs		948s
935m	925m	923s			922m
857vs	847vs	849vs	859vs	863vs	868s, 846vs
832 (sh)	840m	825s	823m	824w	835s
	806m				
	787w	779m	780m	780m	787m
b			601vw	616w	
	583w	567w	568w		568w, 560w
	555w	545w			545w
			523w		532w
	440vw	465w	455w	485w	465w
			427w		405vw
	380w				389w
	315m	345w	328vw	329w	345m
	280w		305w	288w	324w

[a] Substantially identical spectra for X = Cl and X = Br. [b] Poor quality Raman spectrum.

TABLE 4

Symmetrical Raman metal–halogen stretching or related modes ^{a} (cm^{-1})

	Metal and halide in adduct							
					Cd–Br		Cd–I	
	Hg–Cl	Hg–Br	Hg–I	Cd–Cl	solid	soln.^{b}	solid	soln.^{b}
1 : 1 Adducts								
$MX_2\cdot$thf	297	190			144	173 ^{c}	127 ^{c}	138 ^{c}
$MX_2\cdot$dioxan	295 ^{d}	189	145	227 ^{e}	146 ^{e}		112	
$MX_2\cdot$glyme	305	194		242 234	153 152		118	140
$MX_2\cdot$diglyme	311	200	150				113	127
$MX_2\cdot$triglyme	325	204	153				108	129
$MX_2\cdot$tetraglyme	316	196	146		146		106	128
$MX_2\cdot$18-crown-6	308	189	138	272	171	171	119	119
Other adducts								
$2CdX_2\cdot$diglyme$\cdot H_2O$				236	164			
$3CdBr_2\cdot$2diglyme$\cdot 3H_2O$					159			
α-$2CdX_2\cdot$triglyme				235	152			
β-$2CdBr_2\cdot$triglyme					153			
$2CdX_2\cdot$tetraglyme				246	163			
$3CdBr_2\cdot$15-crown-5					155			
Monomeric model compounds								
$MX_2(Bu_3PO_4$ solution) ^{f}	328 ^{g}	203 ^{g}	148 ^{g}	278 ^{g}		189		145
$[MX_3]^{-}$ ^{f,h}	296 ^{g}	187 ^{g}	134 ^{g}	252	164	170	118	127
Halogen-bridged model compounds								
MX_2 (solid)	316 ^{i}	188 ^{i}	141 ^{j}	233 ^{k}	148 ^{k}		114	
$MX_2\cdot$pyrazine ^{e}				215	137		105	

[a] Estimated accuracy ±1 cm^{-1}. Solid-state data unless otherwise noted. [b] In solution in excess of pure ligand, chloroform, or tributylphosphate; similar spectra obtained in acetone solution in several cases. Bands observed to be polarized. [c] K. Cavanagh and R. F. Evans, *J. Chem. Soc.* (*A*), 1969, 2890. [d] Refs. 16*d* and P. Tarte and P. A. Laurent, *Bull. Soc. chim. France*, 1957, **24**, 403. [e] Ref. 28. [f] Ref. 27*b*. [g] Solution data. [h] J. G. Contreras and D. G. Tuck, *Canad. J. Chem.*, 1975, **53**, 3487. [i] E. A. DeCamp, Y. Marqueton, and M. Durand, *J. Mol. Structure*, 1973, **19**, 505. [j] R. P. Cooney, *Austral. J. Chem.*, 1974, **27**, 1555. [k] D. J. Lockwood, *J. Opt. Soc. Amer.*, 1973, **63**, 374.

TABLE 5

Asymmetric metal–halogen stretching or related modes (cm^{-1}) [a]

	Metal and halide in adduct							
	Hg–Cl		Hg–Br		Hg–I	Cd–Br	Cd–I, Raman	
	Raman [a]	i.r.[a]	Raman	i.r.	Raman	Raman	solid	solution [b]
MX_2·thf								198w
MX_2·dioxan		351 [c]					174w	
MX_2·glyme		355 [d]						
MX_2·diglyme	364w	363 [d]	261m	251	212s		155s	151
MX_2·triglyme		368 [d]	248m	249	210m		147vs	145
MX_2·tetraglyme		358 [d]			210w	164m	124m	144
MX_2·18-crown-6		347 [d]						
$MX_2(Bu_3PO_4)$ [e]		366	255vw	254	205vw	230vw		190w
$[MX_3]^-$ [e,f]						201	171	165
						187	162	

[a] Estimated accuracy ±1 cm^{-1}. Solid-state data unless otherwise noted. Method of observation (Raman or i.r.) indicated. Intensities given for Raman data. [b] Solution in excess of ligand (or tributylphosphate). [c] P. Tarte and P. A. Laurent, *Bull. Soc. chim. France*, 1957, **24**, 403. [d] Ref. 3. [e] In tributylphosphate solution; ref. 27*b*. [f] J. G. Contreras and D. G. Tuck, *Canad. J. Chem.*, 1975, **53**, 3487.

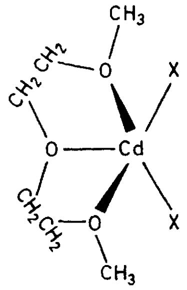
TABLE 6

N.q.r. frequencies (in MHz) of CdX_2 adducts and related compounds at 77 K

			^{127}I [a,d]		
	^{81}Br [a,b]	CN_{Cd} [c]	$m = \pm\frac{1}{2} \rightleftharpoons \pm\frac{3}{2}$	$m = \pm\frac{3}{2} \rightleftharpoons \pm\frac{5}{2}$	CN_{Cd} [f]
1 : 1 Adducts					
CdX_2	14.318 [e]	6	14.752 [f]	29.474 [f]	6
CdX_2·dioxan	54.646(8) [g]	6	125.680(30)		4
			130.289(20)		
CdX_2·glyme	54.000(20)	6	73.618(3)	137.03(6)	6
			75.177(3)	138.08(4)	
CdX_2·diglyme			105.705(40)	208.51(5)	5
			106.303(63)	212.42(6)	
CdX_2·triglyme			107.283(80)	211.25(4)	6
CdX_2·tetraglyme	67.252(8)	7	82.455(4)	164.97(2)	7
	69.730(10)		82.646(5)		
CdX_2·18-crown-6	83.949(14)	8	104.16(8)		8
			105.76(4)		
			106.63(4)		
Other adducts					
CdX_2·2pyridine	40.98 [g]	6	100.08 [g]	199.60	4
			100.41	200.04	
$[p\text{-}ClC_6H_4N_2^+]_2[CdX_4]^{2-}$	62.04(2) [f]	4	85.78(6)		4
	63.41(2)		94.48(3)		
	65.17(2)		98.15(3)		
	68.86(2)				
$2CdBr_2$·diglyme	52.744(25)	5, 6			
	56.872(15)				
$3CdBr_2$·2diglyme·$3H_2O$	49.192(9)	6 [h]			
	50.187(11)				
	50.475(11)				
α-$2CdBr_2$·triglyme	52.395(4)	6			
	52.809(4)				
β-$2CdBr_2$·triglyme	54.436(21)	6			
	54.567(15)				
$2CdBr_2$·tetraglyme	50.345(8)	6 [i]			
	53.198(8)				
	57.514(8)				
	70.093(6)				
^{35}Cl Results	^{35}Cl [a,b]				
$CdCl_2$·18-crown-6	12.802(2)	8			
$RbCdCl_3$	11.23 [j]	6			
$CsCdCl_3$ (D^4_{6h})	6.50 [k]	6			
	11.765				
$CsCdCl_3$ (O^1_h)	11.958 [k]	6			

[a] Signal-to-noise ratio given in parentheses. [b] Error in measurement estimated at ±0.012 MHz. [c] CN_{Cd} = co-ordination number of cadmium, calculated according to the equation in the text. [d] Error in measurement estimated at ±0.025 MHz. [e] Ref. 6. [f] Ref. 8. [g] Ref. 10. [h] Calculated assuming the water is not co-ordinated to cadmium. [i] Actual CN_{Cd} values are 6 and 7, since one oxygen atom co-ordinates to two cadmium atoms (ref. 22*a*). [j] Ref. 9*a*; at 115 °C. [k] Ref. 9*b*; at room temperature.

For some of the compounds, an additional medium-intensity, halogen-dependent band was observed which coincides with the strong M–X stretching frequency found in the i.r. region. These are therefore assigned to the asymmetric M–X stretching vibration, and are tabulated in Table 5 *with* the model spectra. Two possible causes of Raman activity of this band are (*a*) bending of the XMX molecule, or (*b*) inequivalence of the two halogens, as by bridging involving only one of them. We have previously [3] presented n.q.r. evidence suggesting the latter factor for HgX_2·diglyme (X = Cl or Br) and HgX_2·triglyme (X = Br or I), which show this feature in the Raman spectrum. This additional band also appears with low intensity in the spectra of the tetraglyme adducts of HgI_2, $CdBr_2$, and CdI_2, and with high intensity in the spectra of the di- and tri-glyme adducts of CdI_2. These adducts have easily polarizable M–X bonds, and ligands (especially diglyme and triglyme) which must give very asymmetrical co-ordination environments to the metal atoms. Under these conditions bending of the XMX molecule away from the ligand seems reasonable, and is indeed proved in the case of the adduct $Cd[Mn(CO)_5]_2$·diglyme, in which the angle Mn–Cd–Mn is bent to 136°, away from the diglyme ligand [4; X = $Mn(CO)_5$].[25] This structure (4; X = I) is proposed for CdI_2·diglyme. CdI_2·dioxan also shows this feature, and has previously been suggested to have tetrahedral co-ordination about cadmium.[28]



(4)

X = $Mn(CO)_5$, structure known

X = I, structure proposed: $CN_{Cd} = 5$, $CN_I = 1$

Below *ca.* 125 cm^{-1} a number of intense lattice modes were observed in the Raman spectra, but no attempt has been made to tabulate or to interpret these, or many weak bands found below 300 cm^{-1}. For the series CdX_2·glyme (X = Cl, Br, or I), CdX_2·tetraglyme (X = Br or I), and $2CdX_2$·tetraglyme (X = Cl or Br), the M–X stretching and lattice modes did show such similar patterns, shifted to lower frequencies for heavier halogens, as to indicate isomorphous crystal structures.

N.Q.R. Spectra.—In Table 6 are presented the ^{35}Cl, ^{81}Br, and ^{127}I n.q.r. data for the CdX_2 adducts and related compounds. (Unfortunately no spectra were obtained for the thf and 15-crown-5 adducts.) The ^{127}I ($m = \pm 1/2 \rightleftharpoons \pm 3/2$) n.q.r. frequencies of the 1 : 1 complexes are plotted in Figure 1 as a function of n, the number of oxygen atoms in the polyether. As expected,[3] we find a 'double step function,' *i.e.* two jumps to higher frequencies, corresponding to the two changes in the co-ordination number of the halogen (which we symbolize CN_X) from $CN_X = 3$ in CdI_2 (5) to $CN_X = 2$ to terminal halogen, $CN_X = 1$. Beyond the last step we expect a regular decrease in n.q.r. frequency, as the co-ordination number of the metal increases. (The anomalies of the 18-crown-6 n.q.r. frequencies will be discussed later. Parallel behaviour may also be discerned among the ^{81}Br n.q.r. frequencies.) Hence, observing that the first 'step' occurs with the n.q.r. frequencies of $CdBr_2$·glyme, CdI_2·glyme, and $CdBr_2$·dioxan, we propose that the halogens are bridging [$CN_X = 2$; as in CdI_2·glyme (6)] in these compounds, but terminal in the other 1 : 1 adducts.

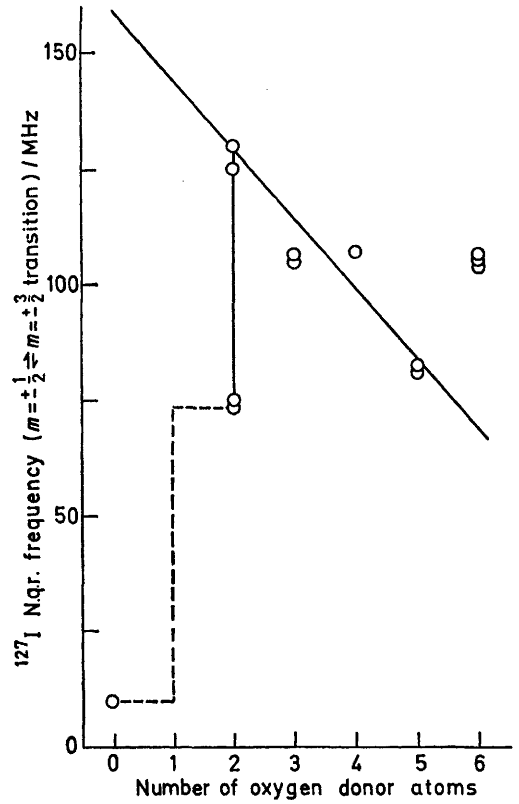
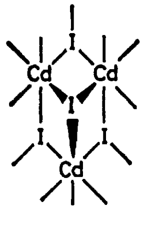


FIGURE 1 ^{127}I n.q.r. frequencies ($m = \pm 1/2 \rightleftharpoons \pm 3/2$) of CdI_2 adducts as a function of n, the number of oxygen donor atoms. Data for $n = 1$ (CdI_2·thf) were not obtained, and are suggested with broken lines. Extrapolation to $n = 0$ (matrix-isolated CdI_2) is shown with a solid line



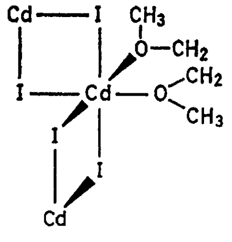
(5) $CN_{Cd} = 6$, $CN_I = 3$

Since no direct structural evidence is available to support these conclusions, one may note other evidence. (i) From the ^{127}I n.q.r. frequencies one may compute much higher asymmetry parameters for CdI_2·glyme than for the other adducts;[23] this suggests bridging halogens.[2] (ii) Allowing

---

[28] M. Goldstein and W. D. Unsworth, *J. Mol. Structure*, 1972, **14**, 451.

for differing ligand basicity, the glyme and dioxan adducts of $CdBr_2$ have comparable n.q.r. frequencies to $CdBr_2$·2pyridine,[10] which is known to have bridging bromines.[29] (iii) Examining the Raman data given in Table 4 and more conclusively the data of Table 5, one notes that the M–X vibrational frequencies of CdX_2·glyme and $CdBr_2$·dioxan resemble those of the model compounds with halogen bridging, while the other adducts resemble the monomeric model compounds. (iv) The Raman and far-i.r. spectra of the dioxan adducts suggest bridging halogen in $CdBr_2$·dioxan but not in CdI_2·dioxan.[28] (v) The lattice modes suggest that the CdX_2·glyme adducts are all of isomorphous crystal structure. But the absence of a Cd–Cl stretching frequency in the far i.r.[16a] above 220 cm^{-1} suggests bridging chlorine.[30]



(6) $CN_{\mathrm{Cd}}=6$
$CN_{\mathrm{I}}=2$

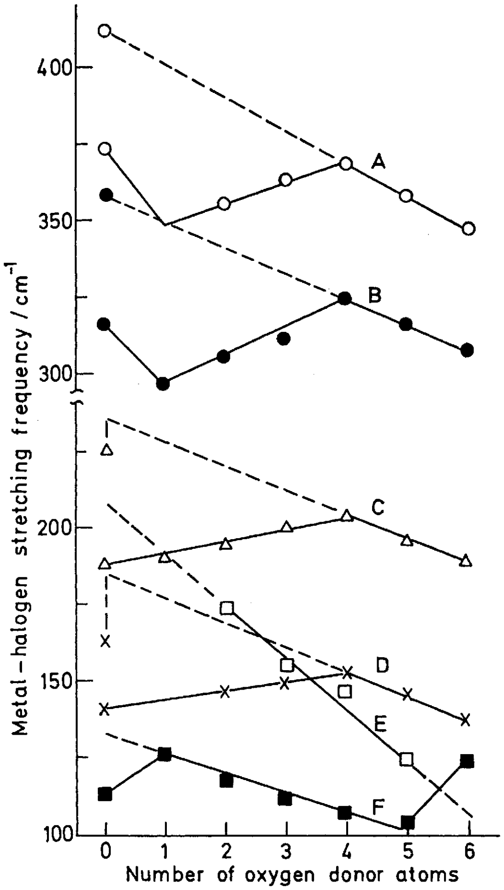


FIGURE 2 Metal–halogen stretching frequencies as a function of *n*. Solid lines indicate trends of actual data; broken lines show extrapolation to matrix-isolated species ($n = 0$). Curve A = antisymmetric Hg–Cl; B = symmetric Hg–Cl; C = symmetric Hg–Br; D = symmetric Hg–I; E = antisymmetric Cd–I; F = symmetric Cd–I stretching frequencies. Broken lines are extended at $n = 0$ to connect with experimental vibrational frequencies [42] of matrix-isolated mercury halides

There is a correlation of the halogen n.q.r. frequencies with the symmetric and asymmetric metal–halogen stretching frequencies of these adducts.[3,31] In Figure 2 these stretching frequencies are plotted as functions of *n* for the 1 : 1 adducts; the maxima in these functions occur at about the same value of *n* as in the n.q.r.-frequency functions in Figure 1 and refs. 3 and 23.

For the 2 : 1 and 3 : 2 adducts of $CdBr_2$, we find remarkable similarity of the n.q.r. frequencies, to each other and to those of $CdBr_2$·glyme and $CdBr_2$·dioxan. The only exception is the one high frequency of $2CdBr_2$·tetraglyme. From the crystal structure of the apparently isomorphous $2CdCl_2$·tetraglyme,[22a] one can assign the high frequency to the one terminal halogen, while all other frequencies in these adducts can be assigned to bridging bromines.

DISCUSSION

Structure and Ligand Basicity.—The weakly basic glyme polyethers are apparently unable to break up completely the halogen bridging found in cadmium chloride and bromide, except in one case ($CdBr_2$·tetraglyme) where the co-ordination number of cadmium (CN_{Cd}) is increased by doing so. With CdI_2, monomeric 1 : 1 adducts are much more readily formed.

If all *n* oxygen atoms in a polyether adduct co-ordinate the metal atom *via* one lone pair of electrons each, we can compute CN_{Cd}:

$$CN_{\mathrm{Cd}} = CN_{\mathrm{X}_1} + CN_{\mathrm{X}_2} + n$$

Using the assignments of CN_{X_1} and CN_{X_2} (for the two halogens) which were made from the n.q.r. data, the values of CN_{Cd} shown in Table 6 are obtained. $CN_{\mathrm{Cd}} = 6$ is computed in most cases for $CdBr_2$ adducts, regardless of the stoicheiometry of the adduct. (This might also be true in $2CdBr_2$·diglyme, if one oxygen atom bridges *via* two lone pairs of electrons, as in $2CdCl_2$·tetraglyme.[22a]) Lower co-ordination numbers for CdI_2 are not unexpected, due to the large size of I, and since crystal-structure determinations show $CN_{\mathrm{Cd}} = 4$ in CdI_2·2aniline [32] and $CN_{\mathrm{Cd}} = 5$ in CdI_2·pyridine *N*-oxide.[33]

For the 2 : 1 and 3 : 2 adducts, the equation must be used with regard to the stoicheiometry, and usually suggests that, on the average, two oxygen atoms are co-ordinated per cadmium atom. Hence it may be the case that *both* ligand and halogen bridge between cadmium atoms in these adducts.

In the previous work [3] on HgX_2 adducts of polyethers,

---

[29] T. I. Malinovskii and Yu. A. Simonov, *Soviet Phys. Doklady*, 1962, **7**, 970.

[30] G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1964, 166.

[31] D. E. Scaife, *Austral. J. Chem.*, 1971, **24**, 1753.

[32] A. B. Ablov and T. I. Malinovskii, *Soviet Phys. Doklady*, 1960, **5**, 467.

[33] G. Sawitzki and H. G. von Schnering, *Chem. Ber.*, 1974, **107**, 3266.

much smaller ' step functions ' were observed in the n.q.r. frequencies than we find here. This will be discussed quantitatively later;[23] but it clearly reflects the weakness of halogen bridging in the mercury halides and their adducts with oxygen bases[34] as compared to cadmium analogues.

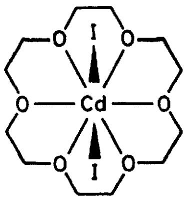
For a given CN_X, one can see the influence of ligand basicity on the n.q.r. frequency: for octahedral $CdBr_2{\cdot}2L$, the less basic ligands (L = dioxan or polyether) lead to higher ^{81}Br n.q.r. frequencies (*ca.* 54 MHz) than does L = pyridine (*ca.* 41 MHz[10]). For tetrahedral $CdI_2{\cdot}2L$ we can compare L = 1/2 dioxan (*ca.* 128 MHz) with L = pyridine (*ca.* 100 MHz[10]) and L = iodide ion (*ca.* 92 MHz[8]).

Interaction of Cd *and the Crown Ether*.—The polyethers and especially the crown ethers have been of intense interest recently[35] because of their resemblance to antibiotics which transport alkali-metal ions across cell membranes. Our observation that some of these cadmium complexes show solubility in solvents of low polarity such as chloroform raises the question as to whether such ligands could perhaps also transport heavy-metal ions.

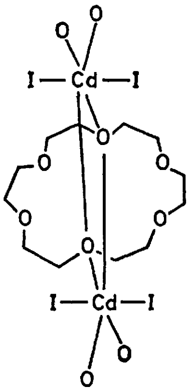
The i.r., Raman, and n.q.r. spectra establish that the ligand 18-crown-6 has the chelating ' crown ' conformation. For all HgX_2 and CdX_2 except CdI_2, there is only one halogen n.q.r. frequency, showing all halogens to sit in crystallographically equivalent positions (unless, because of unfavourable relaxation times, signals have been missed). (The three n.q.r. frequencies of $CdI_2{\cdot}$18-crown-6 fall close together, suggesting that the iodine atoms have only crystallographic non-equivalence.) The i.r. and Raman spectra of the 18-crown-6 adducts are similar to those of the 1 : 1 polyether adducts, and are extremely similar to those of KBr·18-crown-6[35] and $2CH_3CN{\cdot}$18-crown-6,[36] which are inferred to have the crown conformation known to exist in KSCN·18-crown-6.[37a] Mutual exclusion appears to hold between the i.r. and Raman spectra, indicating the presence of an inversion centre.

In (7) and (8) are drawn two possible structures, each of which has the crown configuration and an inversion centre. The symmetry in (8) is lower, and should produce additional vibrational frequencies from the splitting of the E_g (and E_u) modes; since this is not observed, the structure (7) seems likely. In (8) the 18-crown-6 acts as a ' bridging ' ligand, not unlike dioxan; but the temperature-dependencies of the n.q.r. frequencies of the 18-crown-6 adducts suggest chelated, not bridged, ligands.[23] Only one piece of evidence supports the structure (8): from Figure 1 it may be seen that the observed n.q.r. frequencies of ^{127}I (and Br and Cl) are compatible with *four* oxygen donor atoms being co-ordinated to Cd. However, the n.q.r. frequencies[3] of $HgX_2{\cdot}$18-crown-6 strongly suggest *six* oxygen donor atoms, and the two series of adducts have virtually identical ligand vibrational spectra.

Hence the high n.q.r. frequencies in $CdX_2{\cdot}$18-crown-6 are an anomaly. We tentatively propose the structure (7) for both the HgX_2 and CdX_2 adducts: it is completely compatible with the average Hg–O distance of 2.80 Å and O–Hg–O bond angles of 59—63° found in the polyether adducts of $HgCl_2$.[22c] The CdX_2 adducts then must have nearly the same distances and angles, since the crown ether is prevented from contracting by oxygen–oxygen repulsions. But this distance is much larger than the average Cd–O distance of 2.46 Å found in $2CdCl_2{\cdot}$tetraglyme.[22a] [For the same reason, there are unusually long M–O bond distances in NaSCN·dibenzo-18-crown-6[38] and $Ca(SCN)_2{\cdot}$18-crown-6.[37c]] The ^{127}I n.q.r. frequency is *ca.* 40 MHz higher than we would extrapolate (for *n* = 6) from Figure 1, indicating higher Cd–I covalency. Evidently the weak Cd–O interaction is compensated by an unusually strong Cd–halogen interaction.



(7)



(8)

The $CdI_2{\cdot}$18-crown-6 prepared by us has a different i.r. spectrum than that prepared by Knöchel,[20] which showed increased complexity and lower i.r. frequencies in the 1 000—1 100 cm^{-1} region. After a period of time, however, their sample showed i.r. and Raman spectra identical to ours.[39] It appears, then, that two forms of this adduct can exist, with the form reported here being the more stable, and having the structure (7).

To investigate this size disparity further, some preliminary investigations were made on the reactions of CdX_2 with the smaller 15-crown-5, $[CH_2CH_2O]_5$. In thf–diethyl ether solution, a non-stoicheiometric adduct of CdI_2 was obtained. Since its i.r. spectrum showed broad bands, it is not reported here. In contrast, from ethanol solution a $CdBr_2$ adduct was obtained with sharp lines and frequencies similar to those of the chelating adducts (Table 2), suggesting a ' crown '

---

[34] D. Grdenić, *Quart. Rev.*, 1965, 303.

[35] For review articles see J.-M. Lehn, *Structure and Bonding*, 1973, **16**, 1; M. R. Truter, *ibid.*, p. 71; W. Simon, W. E. Morf, and P. Ch. Meier, *ibid.*, p. 113; R. M. Izatt, D. J. Eatough, and J. J. Christensen, *ibid.*, p. 161.

[36] R. D. McLachlan, *Spectrochim. Acta*, 1974, **30A**, 2153.

[37] (*a*) P. Seiler, M. Dobler, and J. D. Dunitz, *Acta Cryst.*, 1974, **B30**, 2744; (*b*) M. Dobler, J. D. Dunitz, and P. Seiler, *ibid.*, p. 2741; (*c*) J. D. Dunitz and P. Seiler, *ibid.*, 2750.

[38] D. Bright and M. R. Truter, *Nature*, 1970, **225**, 176.

[39] G. Rudolph, personal communication.

conformation. It has, however, an unusual stoicheiometry, $3CdBr_2{\cdot}15$-crown-5. Its i.r. and Raman spectra do *not* show mutual exclusion; however, a ring of five oxygen atoms cannot have an inversion centre. No n.q.r. spectrum could be observed over the range of 15—85 MHz; so additional structural conclusions are not possible. In NaI•benzo-15-crown-5,[40] the average Na–aliphatic-O distance is 2.40 Å, less than the Cd–O distance in $2CdCl_2$•tetraglyme.[22b] Since the Na^+ ion is 0.70 Å out of the plane of the crown ether oxygens, we would anticipate the same effect in $3CdBr_2{\cdot}15$-crown-5.

The Matrix-isolated MX_2 *Molecule.*—After excluding adducts with bridging halogens and with the poorly-fitting 18-crown-6, the remaining 1 : 1 polyether adducts form a series in which the co-ordination number of the metal is $n + 2$. It is possible to extrapolate the n.q.r. and vibrational spectra of these to $n = 0$, as a means of estimating the characteristics of a matrix-isolated MX_2 molecule. This seems a reasonable approach to such an estimation, since the polyethers are as weak a class of ligands as are likely to chelate the metal halides, and their small effects should be subtracted by extrapolation to $n = 0$.

Such extrapolations are indicated in Figures 1 and 2. N.q.r. cannot normally be done on matrix-isolated systems, but i.r. and Raman data on matrix-isolated HgX_2 molecules are available.[41a] For $HgCl_2$ the extrapolations reproduce the observed frequencies exactly, but progressively larger deviations are seen for $HgBr_2$ and HgI_2. Several possible reasons for such discrepancies can be anticipated. (i) Some of the adducts may have non-linear metal–halide units, in which case their vibrational frequencies are not true stretching frequencies, and their n.q.r. frequencies may be affected by altered hybridization of the metal atom. (ii) The effect of the adduct lattices and crystal-field effects[42] may not extrapolate to the effect of an inert-gas matrix. (iii) In some cases the matrix-isolated species may not truly be monomeric. (iv) The matrix-isolated species might be multiple-bonded while each of the adducts studied was single (M–X) bonded. Effects (i) and (ii) should become more important with the heavier, more polarizable halogens, as does seem to be observed in Figure 2. Effects (iii) and (iv) suggest reasons why this sort of extrapolation might be valuable for comparison with actual matrix-isolation data.

Extrapolation of the room-temperature n.q.r. data already presented[3] gives 23.9 MHz for $Hg^{35}Cl_2$, 155 MHz for $Hg^{81}Br_2$, and 189 MHz for HgI_2 ($m = \pm 1/2 \rightleftharpoons \pm 3/2$). The only isolated species with which one can compare these data are the gaseous methylmercuric halides. From their quadrupole coupling constants[43] somewhat lower frequencies are computed as would be expected: $CH_3Hg^{35}Cl$, 21 MHz; $CH_3Hg^{81}Br$, 145 MHz. (Microwave data[44] for CH_3HgI give 251 MHz, which seems too high, both with respect to the above data and to the n.q.r. data for solid CH_3HgI.[45] These microwave data for CH_3HgI have been disputed.[46])

Extrapolation of the data for the CdI_2 adducts gives the following estimates: ν (^{127}I, $m = \pm 1/2 \rightleftharpoons \pm 3/2$) *ca.* 160 MHz; * asymmetric Cd–I stretching mode *ca.* 210 cm^{-1}. Steeper slopes increase the uncertainty in the extrapolation. The stretching frequencies are very low, however, and the changes of these frequencies in solution (especially for the symmetric mode) suggest considerable coupling with lattice modes. Hence these extrapolations for CdI_2 in Figure 2 are only approximate. The reported[41b] asymmetric Cd–I stretching frequency for matrix-isolated CdI_2 is 269 cm^{-1}.

Even taking the uncertainties into account, it is apparent that the ^{127}I n.q.r. frequency of an isolated CdI_2 molecule is far higher than that of solid CdI_2, and is not so different from that of isolated HgI_2. Indeed, using these frequencies of isolated molecules, the Townes and Dailey n.q.r. theory[2] with 15% *s*-hybridization of iodine, and Gordy's relationship of electronegativity to ionic character,[2] one may calculate electronegativities for cadmium (1.75) and mercury (1.96) which are comparable with those of Pauling (1.69 and 2.00).[47] The main difference in the two metals seems to arise when additional ligands interact with the isolated MX_2: from the extrapolations it may be computed that each additional oxygen donor atom lowers the CdI_2 n.q.r. frequency by 9.6% but the HgX_2 n.q.r. frequency by only 2.4%. The much stronger Lewis acidity of CdX_2 toward these ligands is then seen. The larger steps in the CdI_2 ' double step function ' may be similarly explained, if one wishes, as a greater tendency of CdI_2 molecules to co-ordinate to each other to give bridge and finally layer structures (*e.g.* solid CdI_2). In further work[23] it is planned to refine this analysis with regard to the n.q.r. spectra of these adducts.

One of us (G. W.) wishes to thank the Alexander von Humboldt Stiftung for a fellowship in support of this work, and Northland College for leave of absence. The work was also supported by the Deutsche Forschungsgemeinschaft. Helpful discussions with Dr. Daiyu Nakamura are acknowledged.

[6/2095 *Received*, 15*th November*, 1976]

---

* Properly speaking not the n.q.r. frequencies but the quadrupole coupling constants[2] for these adducts should be extrapolated. This is possible only for the iodides, using the ^{127}I($m = +3/2 \rightleftharpoons \pm 5/2$) n.q.r. frequencies. Unfortunately these are not available for many of these species (especially at liquid-nitrogen temperature), but the data available[23] indicate that, for the terminal-halogen species being extrapolated, the asymmetry parameter $\eta \leqslant 0.063$ for HgI_2 adducts and $\eta \leqslant 0.110$ for CdI_2 adducts. Under these conditions the difference between the quadrupole coupling constants for iodine and 6.67 $\nu(m = \pm 1/2 \rightleftharpoons 3/2)$ is, at most, 1.5%, which is less than the uncertainty due to the crystal-field effect.[42]

[40] M. A. Bush and M. R. Truter, *J.C.S. Perkin II*, 1972, 341.

[41] (*a*) A. Givan and A. Loewenschluss, *J. Chem. Phys.*, 1976, **64**, 1967; (*b*) A. Loewenschluss, A. Ron, and O. Schnepp, *ibid.*, 1969, **50**, 2502.

[42] A. Weiss, *Fortschr. chem. Forsch.*, 1972, **30**, 1.

[43] W. Gordy and J. Sheridan, *J. Chem. Phys.*, 1954, **22**, 92.

[44] C. Feige and H. Hartmann, *Z. Naturforsch.*, 1967, **22A**, 1286.

[45] E. V. Bryuchova and G. K. Semin, *J.C.S. Chem. Comm.*, 1972, 1216.

[46] C. Walls, D. E. Lister, and J. Sheridan, *J.C.S. Faraday II*, 1975, **71**, 1091.

[47] J. E. Huheey, ' Inorganic Chemistry: Principles of Structure and Reactivity,' Harper and Row, New York, 1972.