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Vibrational Spectra of *catena*-μ-Ethylenediamine Complexes of Zinc(II), Cadmium(II), and Mercury(II) with the Formula $M(en)X_2$

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Raman and infrared spectra were employed to detect the presence of bridging ethylenediamine (C_{2h} symmetry) in a series of compounds with the formula $M(en)X_2$ where M = Zn, Cd, or Hg, en = ethylenediamine, and X = Cl, Br, or SCN. Mutual exclusion of infrared and Raman bands along with other details of the spectra indicate effective C_{2h} symmetry for ethylenediamine in $Cd(en)X_2$ (X = Cl, Br, or SCN) and $Hg(en)X_2$ (X = Cl or Br). The compound $Zn(en)Cl_2$ appears to be a borderline case since several different solid phases were observed, one of which appears to contain bridging ethylenediamine. In an attempt to systematize the results, limits of stability for the bridged ethylenediamine complexes were estimated from relative metal–halogen and μ-ethylenediamine-metal–halogen radii. Compounds with spectra indicative of C_{2h} ethylenediamine symmetry are also those for which the possibility of a stable bridging structure is predicted.

Introduction

Although ethylenediamine (en) is a well-known chelating ligand in coordination chemistry, it sometimes behaves as a bridging ligand with the trans conformation. Besides the metal-bridged ethylenediamine complexes described in a recent review by Nakamoto,[2] who cited mainly structural conclusions from infrared spectroscopy, $[Pt(en)(CH_3)_3]_2(en)I$,[3a] $[Pt(acac)(CH_3)_3]_2en$,[3b] $[Li(en)](en)X$ (X = Cl, Br),[4] and $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$[5] have been found by X-ray diffraction to contain the bridging trans ethylenediamine ligand. Newman and Powell[6] reported on a series of IIb metal chloride–ethylenediamine complexes, $M(en)Cl_2$ (M = Zn, Cd, Hg), for which the infrared spectra are simple by comparison with those for ethylenediamine chelate complexes. They concluded that the ethylenediamine adopts a trans C_{2h} configuration in these compounds. As part of a broad study of ethylenediamine complexes, Krishnan and Plane[7] suggested that C_{2h} symmetry of en in $Zn(en)Cl_2$ is supported by Raman spectroscopy. Their article represents the only reported attempt to apply Raman spectroscopy to this problem; however on closer examination the $Zn(en)Cl_2$ system is found to be more complex than originally supposed. From an analysis of X-ray powder photographs Brodersen has inferred the trans en configuration in $Hg(en)Cl_2$.[8] As pointed out by Krishnan and Plane[7] and Iwamoto,[9] vibrational data indicate that $Zn(en)Cl_2$ and $Cd(en)Cl_2$ should not be formulated as $[Zn(en)_2][ZnCl_4]$ or $[Cd(en)_2][CdCl_4]$ despite formulations of this type in the older literature.[10]

The purpose of this paper is to apply Raman spectroscopy along with infrared spectroscopy to a study of the geometry of ethylenediamine in $M(en)X_2$ complexes. The two techniques are complementary since bridging ethylenediamine with C_{2h} symmetry requires mutual exclusion of the infrared- and Raman-active bands whereas coincidences are expected for the chelating ligand. Another objective is the systematization of the structural results by a model based on consideration of crystal packing.

Experimental Section

Preparation. Procedure i.—To 0.01 mol of MX_2 (M = Zn, Cd; X = Cl, Br, I, SCN) and 0.04 mol of NaX or KX in 50 ml of slightly acidic H_2O, 7 ml of 10% aqueous en solution (0.01 mol of en) was added with vigorous stirring, and a white precipitate formed. After standing overnight in a refrigerator, the precipitate was filtered on a frit, washed with water, and then with acetone. For $Zn(en)Br_2$, $Zn(en)(NCS)_2$, and $Cd(en)I_2$ ethanol was used in place of acetone because of the solubility of these compounds in acetone. The products were dried under vacuum over magnesium perchlorate. The yield is almost quantitative.

Procedure ii.—To 0.01 mol of HgX_2 (X = Cl, Br) in 30 ml of ethanol 0.04 mol of NaCl or KBr in 20 ml of H_2O was added, followed by 7 ml of 10% ethanolic en solution with vigorous stirring. White $[Hg(en)Cl_2]$ or yellow $[Hg(en)Br_2]$ precipitates formed. After standing overnight in the refrigerator, the precipitate was filtered, washed, and dried as in procedure i.

A sample of $ND_2CH_2CH_2ND_2$ (en-d_4) was prepared from the normal isotopic hydrochloride *via* hydrogen exchange with a large excess of $DCl–D_2O$, followed by neutralization with NaOD. The resulting en-d_4 was subsequently used to prepare Cd(en-d_4)Cl_2.

Anal. Calcd for $Zn(C_2H_8N_2)Cl_2$: Zn, 33.64; C, 12.23; H, 4.11; N, 14.27; Cl, 36.11. Found: Zn, 33.6; C, 11.7; H, 4.3; N, 13.7; Cl, 35.8. Calcd for $Zn(C_2H_8N_2)Br_2$: Zn, 22.91; C, 8.42; H, 2.83; N, 9.82; Br, 56.01. Found: Zn, 23.4; C, 8.5; H, 2.7; N, 9.5; Br, 54.3. Calcd for $Zn(C_2H_8N_2)(NCS)_2$: Zn, 27.05; C, 19.88; H, 3.34; N, 23.19; NCS, 49.08. Found: Zn, 26.9; C, 19.3; H, 3.2; N, 22.9; NCS, 48.2. Calcd for $Cd(C_2H_8N_2)Cl_2$: Cd, 46.18; C, 9.87; H, 3.31; N, 11.51; Cl, 29.13. Found: Cd, 46.3; C, 8.7; H, 3.1; N, 10.2; Cl, 28.9. Calcd for $Cd(C_2H_8N_2)Br_2$: Cd, 33.82; C, 7.23; H, 2.44; N, 8.43; Br, 48.09. Found: Cd, 33.6; C, 6.7; H, 2.6; N, 7.9; Br, 49.4. Calcd for $Cd(en)I_2$: Cd, 26.37; C, 5.63; H, 1.89; N, 6.57; I, 59.54; Found: Cd, 24.0; C, 6.8; H, 2.2; N, 7.7; I, 59.5. Calcd for $Cd(C_2H_8N_2)(SCN)_2$: Cd, 38.94; C, 16.64; H, 2.79; N, 19.41; SCN, 40.23. Found: Cd, 38.9; C, 16.1; H, 2.8; N, 19.1; SCN, 39.4. Calcd for $Hg(C_2H_8N_2)Cl_2$: Hg, 60.49; C, 7.24; H, 2.43; N, 8.45. Found: Hg, 60.3; C, 7.2; H, 2.3; N, 8.3. Calcd for $Hg(C_2H_8N_2)Br_2$: Hg, 47.72; C, 5.71; H, 1.92; N, 6.66. Found: Hg, 47.7; C, 5.5; H, 1.6; N, 6.2.

Except for the pale yellow $Hg(en)Br_2$, all compounds were colorless. The powder X-ray diffraction pattern of $Hg(en)Cl_2$ agreed well with that reported by Brodersen.[8] With the exception of $Zn(en)(NCS)_2$ and $Cd(en)I_2$, all compounds gave sharp

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(1) (a) On leave from the University of Tokyo. (b) Fellow of the Alfred P. Sloan Foundation 1967–1969.

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TABLE I

VIBRATIONAL BANDS OF $M(en)X_2$ (en C_{2h} SYMMETRY)

		$Cd(en)Cl_2$		$Cd(en\text{-}d_4)Cl_2$		$Cd(en)Br_2$		$Cd(en)(SCN)_2$[a]		$Hg(en)Cl_2$		$Hg(en)Br_2$		$Zn(en)Cl_2(i)$[c]	
		Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman
MN str[b]	A_g		...		474 w		428 w		...		666 vw?		654 vw?		...
	B_u	499 w		...		444 w		428 m		...		512 w		458 s	
NH_2 rock	A_u	540 s		422 s		541 s		569 s		687 s		662 s		679 s	
	B_g		528 s		418 w		523 s		524 w		561 s		545 s		562 w
CH_2 rock	A_u	771 vw		...		771 vw		778 w		...		789 w		794 w	
	B_g		...		...		956 w		966 vw		933 vw		...		980 w
CN str	A_g		978 m		1049 w?		974 m		974 w		1003 w		996 w	(1016 vw)	1016 m
	B_u	1014 s		1001 s		1014 s		1006 s		1005 s		1002 s		1005 s	
CC str	A_g		1054 s		1023 s		1051 s		1058 s		1040 w		1037 w		1058 s
NH_2 twist	A_u	1097 s		866 s		1093 s		1063 s		1165 s		1143 s		1108 s 1134 w	
	B_g		1161 s		845 w		1149 s		1131 s		1206 s		1183 m		1162 s
CH_2 twist	A_u	...		...		...		...		...		...		...	
	B_g		1275 vw		...		...		1276 vw		1285 vw		...		1194 w
NH_2 wag	A_g		1343 s		1080 s		1341 s		1350 s		1348 s		1346 m		1352 s
	B_u	1334 s		1013 m		1330 s		1335 s		1343 m		1338 s		1331 s	
CH_2 wag	A_g		1392 w		1394 m		1387 w		1389 w		1390 w		1389 w		1396 vw
	B_u	1359 vw		...		1350 w		...		1351 m		1359 w		1377 w	
CH_2 scisson	A_g		1476 w		1469 w		1463 w		1452 w		1482 w		1472 w	(1446 w)	1466 w
	B_u	1481 m		1483 m		1479 s		1471 m		1493 m		1481 m		1475 m	
NH_2 scisson	A_g		1621 w		1315 s		1607 w		1600 w		1602 w		1598 vw	(1577 w)	1577 w
	B_u	1614 s		1196 s		1602 s		1591 s		1610 s		1600 s		1582 s	
CH_2 sym str			2886 m		2896 m		2886 m		2884 m		2907 s		2897 w	2886 m	2890 s
		2904 m		2908 m		2892 m		2895 m		2892 sh		...		2898 m	2898 s
CH_2 asym str		2974 m	2958 s	2980 m	2920 m	2970 s		2965 s		2946 m		2952 sh		2948 m	2946 s
			2920 s		2961 vs	2956 s	2958 s		2947 s		2971 s		2963 s	2960 m	2962 s
NH_2 sym str					2353 s		3167 s	3144 s	...		3125 s		3127 s		3134 m
		3178 s		2356 s		3162 s		3182 s		3128 s		3138 s		3146 s	
NH_2 asym str		3276 s	3265 s	2414 s	2412 s	3256 s	3260 s	3290 s	3268 s	3192 s		3220 s		3238 s	3232 vs
		3298 m	3292 m	2459 s	2455 s	3292 s	3297 s	3304 s	3318 s		3188 s		3211 s	3284 s	3276 s
				2478 m	2474 w										

[a] The bands assigned to SCN group are omitted. [b] Tentative assignment. [c] The spectrum of $Zn(en)Cl_2(i)$ does not conform strictly to C_{2h} selection rules (see text).

powder diffraction patterns, indicating good crystallinity. We had no success in an attempt to index the powder patterns assuming cubic, tetragonal, or hexagonal lattices. The samples melt with or without decomposition at *ca.* 200° and upon cooling have a glassy appearance with a yellow (M = Zn, Cd) or gray (M = Hg) color. $Cd(en)(SCN)_2$, $Cd(en)I_2$, and $Hg(en)Br_2$ give sharp melting points of 193, 197, and 178°, respectively, and have a colorless glassy appearance upon cooling. All samples are sparingly soluble in water but soluble in mineral acids, aqueous ammonia, or excess en.

Three different types of $Zn(en)Cl_2$ were detected by vibrational spectroscopy. The first, $Zn(en)Cl_2$(i), was prepared by procedure i, the second, $Zn(en)Cl_2$(ii) resulted from $Zn(en)Cl_2$(i) after standing at room temperature for 3 months, and the third, $Zn(en)Cl_2$(iii), was prepared as flaky crystals from a methanolic solution containing the equimolar amounts of $ZnCl_2$ and en. While the preparations of $Zn(en)Cl_2$(i) and -(iii) were reproducible, that of $Zn(en)Cl_2$(ii) was not. The powder X-ray diffraction pattern of $Zn(en)Cl_2$(i) disagreed completely with that of $Zn(en)Cl_2$(iii).

Spectroscopic Measurements.—Infrared spectra were recorded with a Beckman IR9 spectrometer on Nujol, Fluorolube, or hexachlorobutadiene mulls of the compounds. Raman spectra were obtained on a SPEX 1400-II instrument which has been described previously.[11] A Coherent Radiation Model 52 Ar ion laser was employed as the excitation source for the pressed-disk samples. High fluorescence was observed for all samples. The intensity of fluorescence decreased considerably after exposure of the sample to the exciting radiation (5145 Å), but prolonged exposure led to decomposition of the compound. Excitation with the 4880-Å line usually resulted in damage to the sample. The spectrum of $Cd(en\text{-}d_4)Cl_2$ was observed for the polycrystalline sample sealed in a glass capillary with the excitation at 4880 Å. High fluorescence of the sample made it impossible to collect usable Raman spectra for $Zn(en)Cl_2$(iii) and $Zn(en)Br_2$. The spectra of $M(en)Cl_2$ also were recorded with a prototype Cary Model 82 laser-Raman spectrophotometer and the agreement between the two instruments was within 3 cm^{-1}.

Results and Discussion

The observed infrared and Raman bands are shown in Table I for the compounds which are thought to have en molecules in C_{2h} symmetry and in Table II for the other compounds. Figure 1 shows the infrared and Raman spectra of $Cd(en)Br_2$ as a typical example in the region from 1700 to 400 cm^{-1}, where most of the ethylenediamine fundamental vibration modes occur.

Assignments.—Assuming the structure of $M(en)X_2$ is similar to that given by Brodersen[8] for $Hg(en)Cl_2$, the unit cell should contain one formula unit of $M(en)X_2$. This structure, which will be discussed later, is a three-dimensional polymer with ethylenediamine in the trans C_{2h} form. Consequently, there should be 18 infrared-active u modes (8 A_u + 10 B_u) and 18 Raman active g modes (11 A_g + 7 B_g) for the $-M-NH_2-CH_2-CH_2-NH_2-M-$ system. Thus, the selection rules require mutual exclusion of infrared and Raman frequencies.

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TABLE II

INFRARED BANDS OF M(en)X_2 (LOW en SYMMETRY)

			Zn(en)Cl_2		
Cd(en)I_2	Zn(en)-(NCS)$_2$[a]	Zn(en)Br_2	iii	ii	i
474 s		468 m	467 m		
484 s		477 s	476 m	473 m	
				482 s	485 s
			503 vw		
	518 s				
532 vw				548 w	
565 vw	592 w				
		601 s	609 s	612 s	
616 s		617 s	622 s	633 s	
			634 s	644 s	
	654 s	654 s	658 s	658 s	
				680 s	679 s
		772 vw			
	782 vw	798 vw		796 w	794 w
857 w			863 vw		
958 s	967 m		966 w		
987 s	1010 s	990 s	992 vw	992 w	
1009 s	1034 s	1007 s	1009 s	1007 s	1005 s
		1018 sh	1017 vw		1016 vw
1062 m	1078 m	1061 w	1065 w	1065 w	
1091 vw					
1110 s	1102 s			1104 s	1108 s
	1123 vw		1132 s	1132 s	1134 vw
	1150 vw	1153 s	1139 s	1139 s	
		1186 w	1185 vw	1184 vw	
1262 w	1274 m		1275 vw		
1278 m	1282 s		1281 vw		
1320 m	1319 m	1337 s	1339 m	1339 s	1331 s
1370 m		1376 m		1374 w	1377 w
1393 m	1390 w	1394 vw	1394 w		
1458 s	1455 w	1456 s	1455 s	1456 m	
					1466 w
		1477 m		1477 m	1475 m
1567 s			1569 s		
		1572 s	1575 s	1575 s	1577 w
1585 s	1581 s			1589 s	1582 s
	1601 m				

[a] The bands assigned to NCS group are omitted.

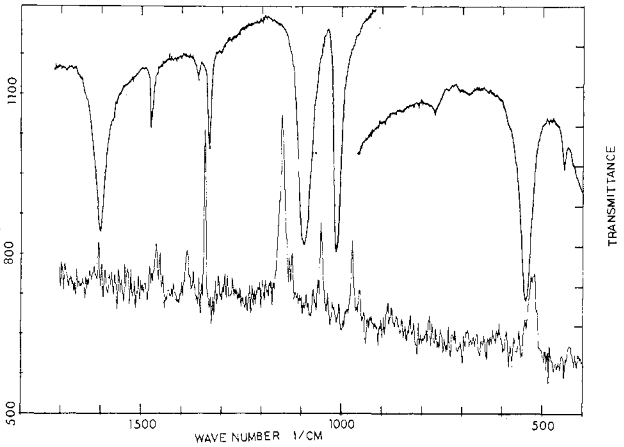

Figure 1.—Infrared (above) and Raman (below) spectra of Cd(en)Br_2. The Raman spectrum was produced from digital data by a Cal-Comp plotting routine.

Each pair of the infrared and Raman spectra observed for the compounds listed in Table I has a pattern similar to that demonstrated for Cd(en)Br_2 in Figure 1. Both frequencies and intensities of the bands showed little variation from one compound to the next. With the exception of a few high-frequency vibrations, the mutual exclusion rule between the infrared and Raman bands is satisfied. These results are consistent with the trans C_{2h} symmetry for the en ligand.

The infrared assignments presented in Table I were facilitated by the observed isotopic shifts between Cd(en)Cl_2 and Cd(en-d_4)Cl_2. Bands assigned to the NH_2 modes were shifted to lower frequency by ratios of ν_{ND_2}/ν_{NH_2} ranging from 0.73 to 0.79. Considering the intensity ratio of the band at 1334 cm^{-1} (NH_2 wag) to that at 1014 cm^{-1} (CN str) for the normal isotopic molecule, the band at 1001 cm^{-1} for Cd(en-d_4)Cl_2 can be assigned to the CN stretching mode and the shoulder-like band at 1013 cm^{-1} to the ND_2 wag.

The Raman spectrum of Cd(en-d_4)Cl_2 is sufficiently complex to preclude detailed assignments. However, it did prove useful since bands which disappeared from the spectrum upon deuteration could be assigned to NH_2 modes of the normal isotopic molecule. The bands tentatively assigned to ND_2 modes decreased upon deuteration by factors ranging from 0.73 to 0.81.

For the C_{2h} en conformation the C–C stretch band is expected to be Raman active only and accordingly is assigned to a band around 1050 cm^{-1} for all the compounds in Table I. Upon deuteration this band appears to shift to 1023 cm^{-1}. Alternatively, either of two weak bands at 1049 and 1089 cm^{-1} for the deuterio compound might be assigned to the C–C stretch. However, intensity considerations strongly favor the 1023 cm^{-1} assignment.

Zn(en)Cl_2, Zn(en)Br_2, Zn(en)(NCS)$_2$, and Cd(en)I_2.—Except for Zn(en)Cl_2(i), the spectra of these compounds were more complicated than those of compounds in Table I. The infrared spectra of Zn(en)Cl_2,[6,7] Cd(en)Cl_2,[6,9] and Hg(en)Cl_2[6,8] and the Raman spectrum of Zn(en)Cl_2[7] have been reported previously, but agreement between the various sets of data is not good. The most striking disagreement occurs for infrared spectra of Zn(en)Cl_2 in the NH_2 rock and NH_2 twist regions. Newman and Powell[6] observed a broad doublet at 630 and 665 cm^{-1} which they assigned to NH_2 rock and a strong band at 1140 cm^{-1} assigned to NH_2 twist. Krishnan and Plane,[7] on the other hand, listed three peaks and a shoulder at 612, 624, 636 (sh), and 660 cm^{-1} assigned to NH_2 rock and a strong band at 1140 cm^{-1} which they assigned as an NH_2 wag mode. These disparities are partially resolved by the observation of three different forms of Zn(en)Cl_2 (see Experimental Section). For the first of these, Zn(en)Cl_2(i), the doublet or multiplet structure in the 600–660-cm^{-1} region was never observed, but this structure was clearly observed for Zn(en)Cl_2(ii), Zn(en)Cl_2(iii), and Zn(en)Br_2. As shown in Figure 2 and Table II, Zn(en)Cl_2(ii) has a spectrum intermediate between that of Zn(en)Cl_2(i) and -(iii). The X-ray powder diffraction lines of Zn(en)Cl_2(ii) are broad and it is therefore difficult to tell if its pattern is distinct from a superposition of the powder patterns of Zn(en)Cl_2(i) and -(iii). The spectrum of Zn(en)Cl_2(iii) closely resembles that reported by Krishnan and Plane. The spectrum of Zn(en)Cl_2(i) resembles that of Newman and Powell; however differences do exist in the region of 1130–1140 cm^{-1}. When a sample of Zn(en)Cl_2(i) is rapidly heated to its melting point and then quenched, a colorless mass Zn(en)Cl_2(iv) is obtained which displays a broad doublet in the vicinity of 650 cm^{-1} and a broad shoulder at 1140 cm^{-1}. This result suggests the occurrence of a thermally induced phase transition. Juding from their complicated infrared spectra, Zn(en)Cl_2(ii–iv) and Zn-

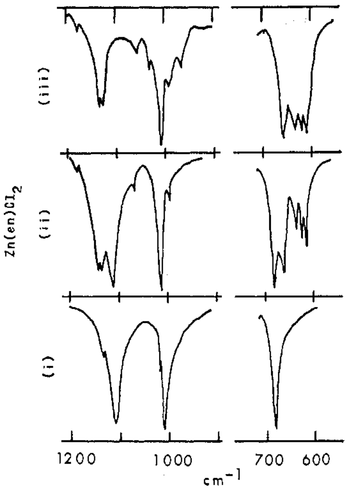

Figure 2.—Comparison of infrared spectra for the three forms of $Zn(en)Cl_2$.

(en)Br_2 contain en in sites of low symmetry.[12] It appears therefore that these compounds are not isostructural with those listed in Table I, which contain en with effective C_{2h} symmetry. A medium to weak band in the infrared which is assigned as C–C stretch is observed in the 1060–1080-cm^{-1} region for each of the compounds listed in Table II except $Zn(en)Cl_2$(i). In the spectrum of $Zn(en)Cl_2$(i) very weak but sharp peaks are present at 1016, 1134, 1466, and 1577 cm^{-1}. Except for the band at 1134 cm^{-1} these infrared bands have counterparts in the Raman spectrum; therefore, the en moiety does not appear to be strictly centrosymmetric. (It is possible, but in our view unlikely, that the coincidences arise from coupling between en groups within the unit cell.) In any case, the gross spectral features indicate an effective trans structure, as previously concluded by Newman and Powell.

The spectrum of $Zn(en)(NCS)_2$ was not interpretable in terms of C_{2h} symmetry for the en ligand. Furthermore, the general features of the spectrum do not resemble those of $Zn(en)Cl_2$(iii) or $Zn(en)Br_2$ but do resemble the $Cd(en)I_2$ spectrum. For example, the medium to strong bands in the 1260–1280-cm^{-1} region observed for $Zn(en)(NCS)_2$ and $Cd(en)I_2$ are not observed for the other compounds in the $M(en)X_2$ series. It is probable that $Zn(en)(NCS)_2$ and $Cd(en)I_2$ contain chelating en since the infrared spectra of en chelate complexes ordinarily have prominent bands with medium to strong intensities in this region.[7,13] Judging from the relative complexity of the thiocyanate modes in the $Zn(en)(NCS)_2$ and $Cd(en)(SCN)_2$ spectra (Table III), the latter compound is more symmetric. This result is consistent with the foregoing conclusions drawn from the en portion of the spectrum.

In summary, vibrational data indicate that the compounds listed in Table II contain en in sites of low symmetry, whereas the compounds listed in Table I contain en in sites of effective C_{2h} symmetry. On this basis, all of the compounds in Table I contain bridging en groups. However, it remains an open question as to whether the compounds in Table II contain bridging en in configurations which are significantly distorted from C_{2h} symmetry or whether the en ligand is nonbridging in these compounds.

TABLE III

VIBRATIONAL BANDS OF SCN IN $Zn(en)(NCS)_2$ AND $Cd(en)(SCN)_2$

	$Zn(en)(NCS)_2$		$Cd(en)(SCN)_2$	
	Ir	Raman	Ir	Raman
NCS bend	477 s	478 m	449 m	444 w
		488 m	465 m	472 m
	826 w	838 s	766 m	767 s
	831 w			
SC str	858 w	879 s		
	870 w			
2(NCS bend)	951 w, sh		896 w	
		973 m	930 w	
	2086 vs, b	2090 s	2110 vs	2104 s
CN str	2102 vs, b	2105 s		
		2117 s		

A Structural Model

On the basis of X-ray powder diffraction data,[8] it is thought that $Hg(en)Cl_2$ crystallizes in a monoclinic space group $P2/m$-$C_{2h}{}^1$ with $a = 5.89$, $b = 4.79$, and $c = 4.38$ Å and $\beta \approx 90°$. Mercury atoms were located from the radial distribution function, and probable chloride positions were obtained from packing considerations. The en ligands were assigned to sites of C_{2h} symmetry on the basis of infrared data and were positioned to maximize hydrogen bonding and minimize repulsion with the chloride ions.[8] While the resulting structure, Figure 3, is somewhat speculative, it is consistent with the vibrational data obtained in the present study for compounds in Table I. The proposed structure has infinite $-MX_2-$ chains with each metal ion coordinated by a square-planar array of four halide ions. Two nitrogen atoms from two different en molecules complete the coordination sphere to yield a trans octahedral geometry around the metal. To avoid tetrahedral distortion of the square-planar array, simple radius ratio arguments require the metal ion to have an ionic radius not less than the minimum radius of the halide cavity, $r_{cav} = (\sqrt{2} - 1)r_{X^-}$. For the chloride ion, r_{cav} is 0.75 Å, which is nearly equal to the ionic radius of divalent zinc, 0.74 Å.[14] The occurrence of

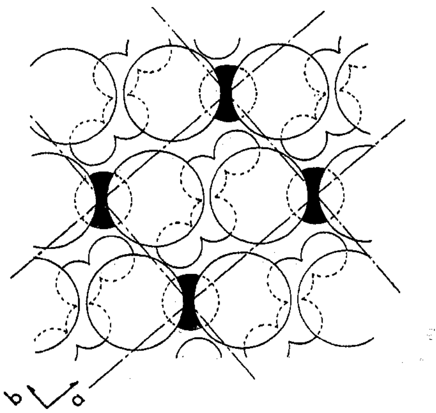

Figure 3.—Projection along the *c* axis of the $Hg(en)Cl_2$ structure proposed by Brodersen.[8] Large circles are Cl, small open circles are N or C, and small closed circles are Hg.

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[12] While the infrared frequencies found for $Zn(en)Cl_2$(iii) and comparable Raman frequencies[7] do not coincide exactly, the largest difference is 9 cm^{-1}, which is far less than observed for en in a C_{2h} environment (Table I) where differences of 30 cm^{-1} are observed in the 1000–1200-cm^{-1} region.

[13] D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 791 (1959); *Spectrochim. Acta*, **17**, 68 (1961).

[14] L. Pauling, "Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1940.

various $Zn(en)Cl_2$ phases, one of which contains nearly C_{2h} en ligands, is consistent with the nearly identical values of $r_{Zn^{2+}}$ and r_{cav}. Similarly, the lack of C_{2h} en ligands in $Zn(en)Br_2$ and $Zn(en)I_2$ is consistent with the values of r_{cav} for bromide and iodide, $r_{cav} = 0.81$ and 0.89 Å, respectively, which are larger than $r_{Zn^{2+}}$.

The r_{cav} values for chloride, bromide, and iodide are satisfactory for cadmium(II) and mercury(II). On this basis, C_{2h} en ligands would be expected for all of these systems. However, one must also consider whether or not en is capable of spanning two metal ions in the lattice. The structure illustrated in Figure 3 may be simplified to a close-packed array of halide ions. For this idealized structure two metal atoms bridged by an en molecule will be separated by 4 times the ionic radius of the halide. A distance of 3.8 Å between two terminal nitrogen atoms of an en molecule in the trans form is calculated assuming a C–C bond length of 1.52 Å, a C–N bond length of 1.47 Å, and bond angles in the NCCN chain of 109.5°. Therefore the minimum possible metal–nitrogen band length is

$$r_{M-N} = {}^1/_2(4r_{X^-} - 3.8)$$

In the real crystal, repulsion between the halide layers leads to a distortion of the crystal away from the close-packed halide configuration and this in turn yields a larger value for r_{M-N} than that calculated by eq 1. For $Cd(en)I_2$ the calculated minimum value of r_{M-N} is 2.4 Å. This is larger than the sum of the Cd(II) and N covalent radii, 2.2 Å.[15] Thus, it appears that en bridging should be energetically unfavorable for the cadmium iodide system. For the other cadmium halides and the mercuric halides the metal ions may approach sufficiently close to give reasonable metal–nitrogen bond lengths. Consistent with these estimates is the observation of effective C_{2h} symmetry for en in the cadmium and mercuric halide systems with the exception of $Cd(en)I_2$.

Octahedral coordination around a mercury(II) atom is occasionally compressed with two shorter and four longer mercury–ligand atom distances.[16] For the present mercury compounds, the compression along the N–Hg–N axis is suggested from the high frequency of the NH_2 rocking bands, which are observed at 687 and 662 cm^{-1} for $Hg(en)Cl_2$ and $Hg(en)Br_2$, higher by *ca.* 120–154 cm^{-1} than those observed for $Cd(en)Cl_2$ and $Cd(en)Br_2$, respectively. The hypothetical model proposed by Brodersen[8] for $Hg(en)Cl_2$ with the Hg–N bond length 2.18 Å and the Hg–Cl bond length 2.9 Å is reasonable in this sense.

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[15] The Cd–N(en) bond length 2.26 ± 0.05 Å has been reported for $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$ in which the en bridges between two cadmium atoms, and a Cd–N(NH_3) bond length of 2.31 Å has been reported for $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$. In each of these compounds, the cadmium atom occupies an octahedral site with trans $CdN_2N_4(NC)$ coordination. *Cf.* ref 5 and Y. Sasaki, *Bull. Chem. Soc. Jap.*, **42**, 2412 (1969).

[16] D. Grdenić, *Quart. Rev., Chem. Soc.*, **19**, 303 (1965).

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Kinetic Study of the Chromium(II) Reductions of Oxalatotetraammine- and Maleatopentaamminechromium(III)

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The reduction of oxalatotetraamminechromium(III) by chromium(II) obeys the rate law $-d \ln [(NH_3)_4CrC_2O_4^+]/dt = 6.37 \times 10^{-3}[Cr^{2+}]$ at 25° and 1.0 M ionic strength, with $\Delta H^{\ddagger} = 12.6 \pm 0.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = -26.7 \pm 3$ cal mol^{-1} deg^{-1}. The analogous reduction of maleatopentaamminechromium(III) obeys the rate law $-d \ln [(NH_3)_5Cr(mal)]_{total}/dt = (k_1 + k_2'[H^+]^{-1})[Cr^{2+}]$. At 25° in 1 M $LiClO_4$ $k_1 = 1.79 \times 10^{-2}$ M^{-1} sec^{-1} and $k_2' = 1.50 \times 10^{-3}$ sec^{-1}. The acid dissociation constant, K_a, of $(NH_3)_5CrO_2CCH{=}CHCO_2H^{2+}$ has been determined between 0 and 30° in 1 M $LiClO_4$. At 25°, $K_a = 1.89 \times 10^{-3}$ M with $\Delta H° = 5.3 \pm 0.3$ kcal mol^{-1} and $\Delta S° = 5.3 \pm 1$ cal mol^{-1} deg^{-1}. The specific rate constant for reduction of the unprotonated form of the complex, k_2, is calculated as 0.795 M^{-1} sec^{-1} with $\Delta H_2^{\ddagger} = 3.4 \pm 2$ kcal mol^{-1} and $\Delta S_2^{\ddagger} = -48 \pm 6$ cal mol^{-1} deg^{-1}. The activation parameters for k_1 are $\Delta H_1^{\ddagger} = 10.4 \pm 0.7$ kcal mol^{-1} and $\Delta S_1^{\ddagger} = -32$ cal mol^{-1} deg^{-1}. These results are compared to previous work on the analogous amminecobalt(III) and aquochromium(III) systems. It is concluded that rate comparisons for the latter two systems are not necessarily reliable in differentiating radical ion and resonance-exchange mechanisms. Differences in the activation parameters indicate that different rate-controlling steps are involved when the oxidizing center is chromium(III) or cobalt(III).

Introduction

Oxidation–reduction reactions in which the electron transfer occurs through a bridging group have been widely studied and the field has been reviewed recently by Gould and Taube.[1] Two limiting cases have been proposed for this type of electron transfer. In the superexchange or resonance-transfer mechanism an electron is transferred from the reducing agent to the bridging ligand while an electron is simultaneously transferred from the bridging ligand to the oxidizing agent. In the chemical or radical ion mechanism the bridging

[1] H. Taube and E. S. Gould, *Accounts Chem. Res.*, **2**, 321 (1969).