

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK**Raman and Infrared Spectra of Complexes of Ethylenediamine with Zinc(II), Cadmium(II), and Mercury(II)¹**

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Raman and infrared spectra were measured for solid ethylenediamine and its tris complexes of Zn(II), Cd(II), and Hg(II) and for solid $Zn(en)Cl_2$. The tris complexes, at least for Zn and Hg, have D_3 symmetry with octahedral coordination of the metal ions. $Zn(en)Cl_2$ has a spectrum consistent with a structure in which ethylenediamine molecules bridge adjacent Zn(II) atoms. Raman spectra were measured for solutions containing all three metal ions with coordinated ethylenediamine. In all cases, both the tris complex and the bis complex were found. For Hg(II), the association constant linking the two was measured to be 0.3. No evidence was found for any case of monodentate ethylenediamine. For the tris complexes, frequency assignments were made on the basis of Raman spectra obtained in both normal and deuterated water.

Nakamoto² has recently reviewed the infrared spectra of metal-ethylenediamine (en) complexes. Detailed vibrational assignments are available for a large number of metal-ethylenediamine complexes from a study of the infrared spectra of the solid complexes and their deuterated analogs.^{3,4} The Raman spectra of anhydrous and aqueous ethylenediamine has been studied recently by Ghazanfar, *et al.*⁵ The only Raman study of the metal-ethylenediamine complexes in solution seems to be that of Mathieu⁶ in 1937 which covered Zn, Pt, Rh, Ir, and Ni. Hence, it was thought worthwhile to reexamine the Raman spectra of some metal complexes of ethylenediamine in aqueous solution. Accordingly, we have studied the Raman spectra of H_2O and D_2O solutions containing the ethylenediamine complexes of Zn(II), Hg(II), and Cd(II). During the course of the study, we have also prepared the following compounds and recorded their infrared and Raman spectra: $Zn(en)_3Cl_2$, $Cd(en)_3Cl_2$, $Hg(en)_3SO_4$, $Hg(en)_3(NO_3)_2$, and $Zn(en)Cl_2$.

Experimental Section

The ethylenediamine used in the studies was originally 98% pure (supplied by Eastman Kodak Co.). The sample was purified by distillation and also by fractional freezing. Even so, the final product contained traces of water. The metal salts used were all of analytical reagent grade purity.

When attempts were made to prepare metal-ethylenediamine solutions containing metal to ethylenediamine ratios 1:1 and 1:2, white insoluble precipitates were obtained in all cases. A clear solution could be obtained only when the metal to ligand ratio was 1:3 or more. So, various solutions were made up which contained different amounts of ethylenediamine in excess of the above ratio.

The solid, trisethylenediamine-metal complexes were prepared by dissolving $ZnCl_2$, $CdCl_2 \cdot 2.5H_2O$, $Hg(NO_3)_2 \cdot H_2O$, and $HgSO_4$ in excess ethylenediamine. On standing, the solutions yielded colorless crystals. The zinc and cadmium salts were re-

crystallized from water. $Zn(en)Cl_2$ was prepared by dissolving 10 g of $ZnCl_2$, 9.10 ml of 98% ethylenediamine, and 4 ml of concentrated (11.51 M) hydrochloric acid in water, the resulting solution being made up to 65 ml. On standing, colorless crystals precipitated, which were almost insoluble in water. The compounds were analyzed for carbon, nitrogen, hydrogen, and chlorine.

Anal. (a) Calcd for $Zn(C_2N_2H_8)_3Cl_2 \cdot 2H_2O$: N, 23.84; C, 20.42; Cl, 20.12; H, 8.00. Found: N, 23.81; C, 20.48; Cl, 18.40; H, 8.17. (b) Calcd for $Cd(C_2N_2H_8)_3Cl_2 \cdot H_2O$: N, 22.03; C, 18.87; H, 6.87. Found: N, 21.63; C, 18.92; H, 7.13. (c) Calcd for $Hg(C_2N_2H_8)_3SO_4$: N, 17.62; C, 15.10; H, 5.07. Found: N, 17.69; C, 15.38; H, 5.31. (d) Calcd for $Hg(C_2N_2H_8)_3(NO_3)_2 \cdot H_2O$: N, 21.44; C, 13.77; H, 5.01. Found: N, 21.25; C, 14.23; H, 5.02. (e) Calcd for $Zn(C_2N_2H_8)_3Cl_2$: N, 14.30; C, 12.25; Cl, 36.18; H, 4.11. Found: N, 14.26; C, 12.32; Cl, 29.73; H, 4.16.

The Raman spectra were recorded using a Cary Model 81 Raman spectrophotometer. The infrared spectra in the region 400–4000 cm^{-1} were recorded using a Perkin-Elmer 337 grating infrared spectrophotometer. The spectra were recorded both in KBr pellets and in Nujol mulls. The two series of spectra were identical. The infrared spectra below 400 cm^{-1} were recorded using a Perkin-Elmer 521 grating infrared spectrophotometer, the sample being pressed into a KI pellet. The mercury complexes, however, seemed to undergo reaction when pressed into KI pellets, and so their spectra were not recorded below 400 cm^{-1} .

Results

The Raman spectra of ethylenediamine and concentrated solutions of $ZnCl_2$ -en and $CdCl_2$ -en containing ethylenediamine in excess of three times the metal ion concentration are reproduced in Figure 1. As can be seen, most of the ethylenediamine lines are shifted in the metal-ethylenediamine solutions, indicating coordination to the metal ions. Table I gives the frequency of the Raman lines of ethylenediamine and solutions of $ZnCl_2$ -en, $CdCl_2$ -en, and $Hg(NO_3)_2$ -en. For free ethylenediamine in H_2O , the values obtained agree well with those of ref 5, which are therefore listed in Table I. The table also lists Raman frequencies observed in D_2O . Although the lines are listed in order of frequency for H_2O , shifted lines in D_2O are listed with the corresponding line in H_2O . It should be noted that use of D_2O as solvent causes isotope substitution in the NH_2 groups but not in the CH_2 groups. For these solu-

(1) Supported by the Office of Saline Water, U. S. Department of the Interior; presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

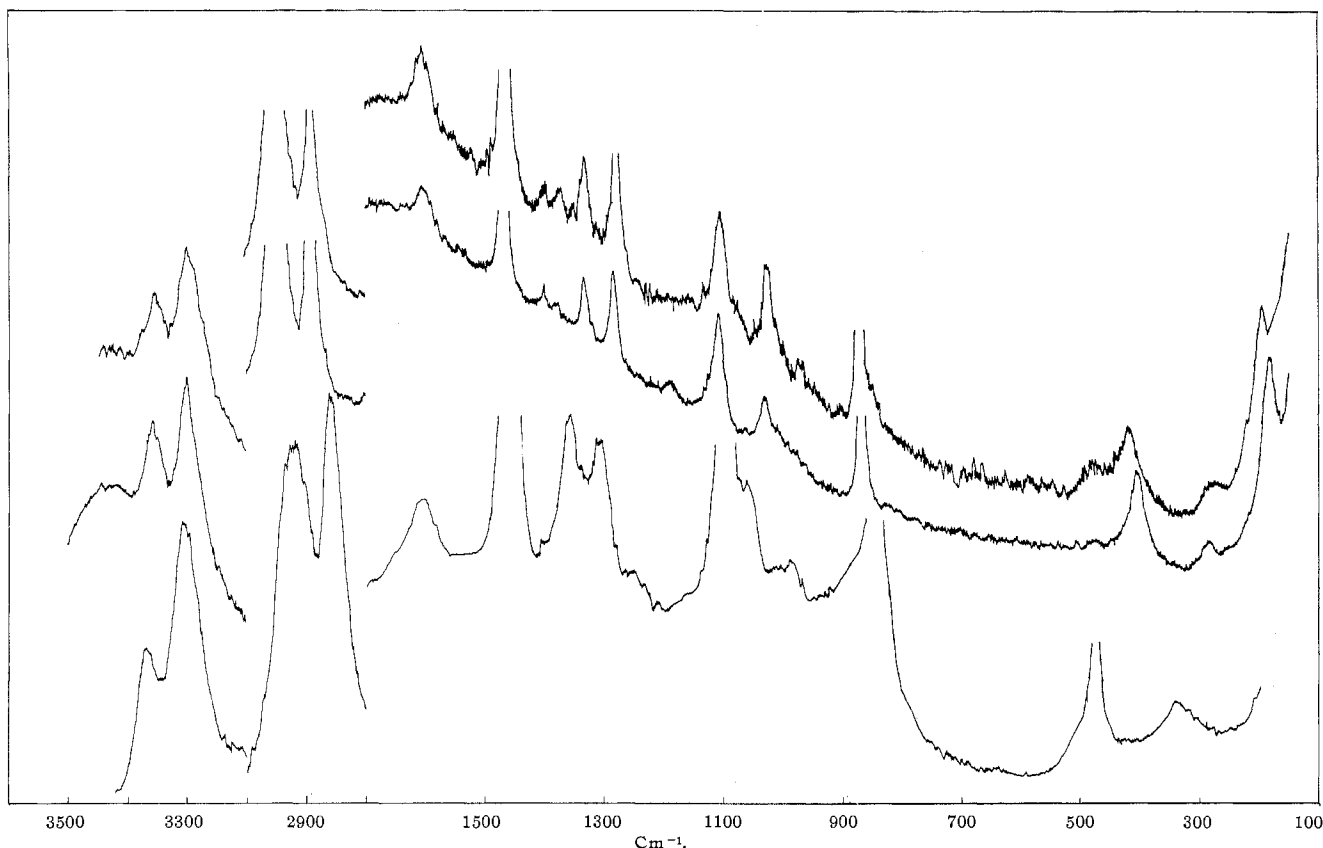
(2) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

(3) D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **17**, 68 (1961).

(4) A. D. Allen and C. V. Senoff, *Can. J. Chem.*, **43**, 888 (1965).

(5) S. A. S. Ghazanfar, J. T. Edsall, and D. V. Myers, *J. Am. Chem. Soc.*, **86**, 559 (1964).

(6) J. P. Mathieu, *J. Phys. Radium*, **8**, 169 (1937).

Figure 1.—Raman spectra of aqueous solutions of $\text{Zn}(\text{en})_3^{2+}$, $\text{Cd}(\text{en})_3^{2+}$, and pure en.TABLE I
RAMAN SPECTRA OF ETHYLENEDIAMINE AND ITS METAL COMPLEXES IN WATER AND HEAVY WATER^a

en		Zn-en		Cd-en		Hg-en		Approx description
H ₂ O	D ₂ O	H ₂ O	D ₂ O	H ₂ O	D ₂ O	H ₂ O	D ₂ O	
...	...	200 m, sh, p	212 m	180 m, p	175 m	198 m, sh, p	192 s	Chelate ring bend
...	...	280 w, b, p	275 w	285 w, p	270 w, b, sh	300 w, b, p	275 w	Chelate ring bend
...	...	423 m, p	405 m, b, p	400 s, p	370 m, b, p	422 s, p	400 s, b	M-N str (tris complex)
...	...	450 p	...	435 p	...	450 p	...	M-N str (bis complex)
477 p	455 m, b	480 w	...	480 w	...	480 w, b	...	Skeletal bend
844 p	820 vw, b	878 s	792 s, p	865 s, p	768 s, p	870 m, p	780 s	
950 b	785 w, b	975 w	815 m	1000 w, sh	810 m, sh	1000 w, sh, dp	795 sh	NH ₂ twist
1013 b	...	1028 m, b	1025 w	1025 m, dp	1025 vw, sh	...	1025 w?	C-N str
1090 p	1065 m, b	1110 m	1054 m, b	1105 s, p	1070 m, b	1100 s, p	1065 m, b	C-N str
...	925 w	...	890 m	1125 vw	890 m	...	890 m	NH ₂ twist
...	1196 w, b	1195 vw	1195 m	1180 vw	1190 m, b	1180 w, b	1190 w, b	CH ₂ twist
1320 dp	1300 m	1285 m	1272 s	1280 s, dp	1275 s	1280 m, dp	1282 s	CH ₂ twist
1362 dp	1065 m, b	1335 m	1054 m, b	1330 m, dp	1048 w, sh	1330 m, dp	1065 m, b	NH ₂ wag
...	1370 w	1380 w	1375 w	1375 w, dp	1375 w	1370 w, dp	1365 w	CH ₂ wag
...	...	1400 w, b	...	1400 w	...	1400 w, b	...	CH ₂ wag
1464 dp	1455 s	1469 vs	1465 s	1466 vs, dp	1463 s	1463 vs, dp	1462 s	CH ₂ bend
...	...	1535 vw, b	...	1535 vw, b	...	1540 vw, b	...	NH ₂ bend?
1602 dp	1196 w, b	1604 m	1195 m	1600 m, b, dp	1190 m, b	1600 m, b, dp	1190 w, b	NH ₂ bend
2885 dp	2875 s	2895 s	2898 s	2890 s	2898 s	2890 s	2894 s	CH ₂ str
2950 p	2945 vs	2955 vs	2963 vs	2950 vs	2955 vs	2954 vs	2952 vs	CH ₂ str
...	2350 m, sh	...	2365 m, sh	2370 w, sh	ND ₂ str
3316 p	2450 s, b	3300 s	2425 s	3300 s	2430 s	3310 s	2450 b	NH ₂ str
3377 dp	2515 m	3353 m, b	2500 s	3355 m	2510 s	3365 m	2508 s	NH ₂ str

^a s = strong; sh = shoulder; b = broad; m = medium; w = weak; vw = very weak; vw? = very weak, doubtful; p = polarized; dp = depolarized. Frequencies are in cm^{-1} .

tions, substitution at NH_2 was essentially complete as shown by the great reduction in intensity of NH_2 lines in the 3300-cm^{-1} region. It is in this region that the largest isotope shifts occur; however, there are also changes noted at lower frequencies. This is particu-

larly true for lines which in ordinary water occur near 1600, 1350, and 975 cm^{-1} . In addition new lines appear near 2350 and 900 cm^{-1} , and there are minor shifts of practically all the lines.

The Raman spectra of the solids are almost identical

TABLE II
RAMAN AND INFRARED SPECTRA OF SOLID ETHYLENEDIAMINE AND THE
SOLID TRIETHYLENEDIAMINE COMPLEXES OF Zn^{2+} , Cd^{2+} , AND Hg^{2+} ^a

Solid en		$Zn(en)_3Cl_2 \cdot 2H_2O$		$Cd(en)_3Cl_2 \cdot 2H_2O$		$Hg(en)_3(NO_3)_2 \cdot H_2O$ ^c	
Raman	Infrared ^b	Raman	Infrared	Raman	Infrared	Raman	Infrared
...	...	200 w, sh	...	180 vw, sh
...	...	275 vw, b	283 w	275 w	282 w	280 m, b	...
...	...	380 w, sh	395 w	385 m, sh	380 w	385 sh	...
...	...	420 m	...	408 s	...	410 s	...
465 m	468 m	450 w	...	450 w	434 w	450 w	450 m, sh
...	...	465 w	...	470 w
...	...	490 w	488 m	485 w	480 m, sh	490 w, b	...
...	515 m	...	496 s	...	500 vs
...	557 w	...	585 sh
...	644 m, b	...	622 s, b	...	652 vs, b
...	698 w, b	...	693 w, b	...	695 w, sh
...	761 s	...	820 vw	...	820 w	...	822 w
...	775 s	...	861 w
...	980 m	875 s	872 vw	865 s	869 m	872 m	...
...	920 vs	...	977 s	...	967 vs	...	985 w
...	996 s	...	998 vs	...	945 vs
1050 m	1065 s	1030 m, b	1022 vs	1025 m, b	1028 s	...	1012 vs
...	1065 b, sh	1060 vw	1056 sh
...	1092 w	1085 w, sh
1106 s	1104 m	1110 m	1107 w	1104 m	1101 m	1104 w	1098 m
...	1144 m, b	1150 w?	1134 s	1155 w	1126 s
1281 m	1298 m	1275 m	1272 m	1280 m	1282 m	1280 w	...
...	1305 m	...	1290 w
1345 m	...	1335 w	1335 m	1333 m	1338 m	1340 sh	1335 m
1368 w	1376 w	1375 vw	1375 w	1375 w	1378 w
1380 vw	...	1400 w	1400 w	1400 m, b	1397 m
1445 m	1456 m	1468 s	1460 m	1465 m	1455 m	1465 m	1475 m, sh
...	1469 m	1480 m	1490 sh	1480 m	1478 m	...	1490 m
...	1500 m
...	1597 m	...	1595 s	...	1568 s	...	1580 s
1598 m	1608 s	1600 s, b	1605 s	1604 m, b	1604 s	1604 m, b	1600 sh
...	1628 s, sh
...	1653 s, sh	...	1675 m	...	1650 w, sh
2852 s	2858 s	...	2882 s	...	2870 s	2885 s	2865 m
...	2880 sh
2900 vs	2917 s	2915 s	...	2925 m
2923 m	2930 s	2945 s	2940 s	2945 s	2930 s, sh	2930 s	2945 m
...	3150 s	...	3140 s	...	3090 vs
3165 m	3171 s	...	3210 sh	3175 s
3247 m	3246 s	...	3235 vs	...	3240 vs	...	3235 vs
...	3275 vs	...	3280 vs	...	3265 vs
3330 vs	3335 s	...	3324 vs	...	3335 vs	...	3310 vs
...	3385 sh	...	3355 s, sh
...	3465 s	...	3460 m, sh	...	3420 m, sh

^a s = strong; m = medium; w = weak; vs = very strong; vw = very weak; sh = shoulder; b = broad. Frequencies are in cm^{-1} .
^b Values taken from ref 7. Full spectrum is not reported here. ^c Identical spectrum for $Hg(en)_3SO_4$; anion frequencies omitted.

with the spectra of the concentrated solutions. The frequency shifts of the Raman lines of the solids and the infrared absorption frequencies are reproduced in Table II. The values for the mercury complexes are the values of both the sulfate and nitrate salts. Except for the anion lines (omitted), these two spectra are identical. Table III gives the Raman and the infrared spectra of $Zn(en)Cl_2$.

Discussion

The Ethylenediamine Molecule.—For molecules as complicated as either ethylenediamine, or particularly its complexes, the assignment of empirical group frequencies is at best a difficult procedure. Most of the descriptions listed in Table I are based on the assignments made by Sabitini and Califano based on infra-

red spectra of normal and N-deuterated ethylenediamine in the gaseous, liquid, and solid states.⁷ We have listed no assignment for the strong polarized Raman line at 844 cm^{-1} in normal ethylenediamine. This line has previously been assigned⁷ to a monohydrate; however, it apparently persists in the pure base.⁵ We find that the line persists in the complexes in both solution and solids. In solid ethylenediamine, the line disappears in both the Raman and infrared.⁷ In D_2O , the line shifts to somewhat lower frequency but by too small an amount to indicate that it is a pure NH_2 mode. It seems likely, for the complexes at least, that it represents a vibration arising from a coupling of skeletal stretching and NH_2 modes. There is also some ques-

TABLE III
RAMAN AND INFRARED SPECTRA OF SOLID $Zn(en)Cl_2^a$

Raman, cm ⁻¹	Infrared, cm ⁻¹	Assignments	
283 s	265 ?	Chain skeletal bend?	
	285 s	Zn-Cl sym str	
	315 s	Zn-Cl antisym str	
	405 m	Chain skeletal bend	
	468 m	Chain skeletal bend	
	480 m	Chain skeletal bend	
	612 s	NH ₂ rock	
	624 s	NH ₂ rock	
	636 sh	NH ₂ rock	
	660 s	NH ₂ rock	
	765 vw	CH ₂ rock	
		775 vw	CH ₂ rock
	820 vw?		C-C str
		988 m, sh	NH ₂ twist
1000 m, b	1006 s	C-N str	
1060 m	1060 w	C-N str	
	1140 s, b	NH ₂ wag	
1190 m	1182 w	CH ₂ twist	
	1285 vw	CH ₂ twist	
1360 w, b	1353 s	NH ₂ wag	
	1380 w	CH ₂ wag	
1400 w, b		CH ₂ wag	
1450 w	1460 s	CH ₂ bend	
1490 w		CH ₂ bend	
1580 m	1580 ^b s	NH ₂ bend	
1600 w, b?	1600 w, sh	NH ₂ bend	
	2865 w	C-H str	
	2915 sh	C-H str	
	2940 m	C-H str	
	2984 w	C-H str	
	3105 w	N-H str	
	3215 s	N-H str	
	3275 s	N-H str	
		3420 w, b	N-H str

^a s = strong; m = medium; w = weak; vw = very weak; sh = shoulder; ? means doubtful; b = broad.

tion concerning the 1362-cm⁻¹ line. This has been previously assigned to CH₂ twisting. However, the present Raman results show that on N-deuteration, the line shifts to 1065 cm⁻¹ indicating that NH₂ is involved in the vibration. With the shift of this line, a weak line remains at 1370 cm⁻¹ which can be assigned to CH₂ motion. Similar conclusions are drawn from isotope substitution in the complexes.

The new line which appears on deuteration at 2350 cm⁻¹ can be an N-D stretching vibration. The corresponding N-H frequency would lie near 3200 cm⁻¹ where it would probably be covered up by the broad H₂O band. In the solid, however, three N-H frequencies are observed at 3330, 3247, and 3165 cm⁻¹. The new line that appears at 925 cm⁻¹ on deuteration should have its NH₂ counterpart near 1100 cm⁻¹ which would be masked by the strong line at 1090 cm⁻¹.

The Raman spectrum of solid ethylenediamine listed in Table II is seen to coincide closely with the infrared spectrum. This is consistent with the earlier assignment of C_{2v} molecular symmetry for the ethylenediamine molecule in the solid.

Complexes in Solution.—Almost all of the Raman lines of free ethylenediamine shift in frequency when it is dissolved along with the metal salts in solution.

As can be seen from Table I, the shifts are considerable, and so it is easy to identify the coordinated ligand. In very concentrated solutions of the complexes (*i.e.*, solutions containing excess ethylenediamine and only small amounts of water) there are two new Raman lines at 423 and 200 cm⁻¹ for the zinc (chloride) solutions; for cadmium (chloride) solutions, there are two new Raman lines at 400 and 180 cm⁻¹; for the mercury (nitrate or sulfate) solutions there are two new lines at 422 and 198 cm⁻¹. All these lines are strong and polarized, and show but small isotope shifts on N-deuteration.

The Raman spectra of the solid tris complexes of these salts have these lines with the same relative intensities and almost the same frequencies as the corresponding solutions. The infrared and Raman spectra of most of the solids (see below) are characteristic of octahedral coordination with molecules having symmetry D₃. It is therefore reasonable to conclude that the species in solution giving rise to these lines are also the trisethylenediamine-metal ions. Then, the two polarized Raman lines must belong to the species A₁, the higher wavenumber one due to the metal-nitrogen stretching vibration and the lower one due to the metal-nitrogen bending vibration. The absence of the anti-symmetric frequencies may mean either that they are too weak to be observed or that they are coincident with the symmetric ones. The concentrations of the metal ions in the above solutions were 1 M or greater and the ethylenediamine concentrations varied from 5 to 10 M.

When the above solutions were diluted, some striking changes were observed. For the mercury salt solutions, on dilution to half the original concentration, the 422-cm⁻¹ Raman line decreased in intensity, and a new line appeared at 450 cm⁻¹, which was also polarized. In the rest of the spectrum, the Raman lines due to free ethylenediamine began to increase in intensity relative to coordinated ligand. On further dilution, the 422-cm⁻¹ line completely disappeared, giving way to the 450-cm⁻¹ one. Similarly for the zinc and cadmium solutions, when the solutions were diluted tenfold, the 423- and 400-cm⁻¹ lines gave way to lines at 450 and 435 cm⁻¹, respectively. However, in these cases, the lower frequency lines did not disappear completely.

When the solid trisethylenediamine complexes were dissolved in water and their spectra recorded in very concentrated solutions, the spectra were identical with those of the original solutions (1 M or more) before dilution. When the crystals were dissolved to give dilute solutions, it was found that in these cases also, the metal-nitrogen stretching frequencies which were originally at 423, 400, and 422 for zinc, cadmium, and mercury solutions, respectively, shifted to 450, 435, and 450 cm⁻¹, respectively.

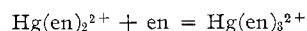
The stepwise formation constants for ethylenediamine complexes with Zn²⁺, Cd²⁺, and Hg²⁺ as given the literature⁸ are (given as log K₁, log K₂, and log K₃):

(8) L. G. Sillén and A. E. Martell, "Stability Constants of Metal Ion Complexes with Solubility Products of Inorganic Substances," 2nd ed, Special Publication No. 17, The Chemical Society, London, 1964.

Zn²⁺, 6.00, 4.81, and 2.17; Cd²⁺, 5.84, 4.78, and 2.07; and Hg²⁺, log $\beta_2 = 23.18$.

It is seen that the formation constant for the tris complex from the bis complex is comparatively low for Zn²⁺ and Cd²⁺. Although no direct determination of K_3 has been reported for the case of Hg²⁺ + en, a value of log $\beta_3 = 23.06$ is listed.⁸ From this value and that of log β_2 , it is seen that K_3 is apparently less than unity. The situation met with in our case seems to be very similar. Since the bis complex is fairly stable in all of these cases, it is reasonable to assume that the new Raman line which appears on dilution is due to the bis complex species.

Two solutions were prepared containing mercuric nitrate and ethylenediamine, one (1.98 *M* Hg(II) and 13.8 *M* en) containing practically only the 422-cm⁻¹ Raman line and the other (0.198 *M* Hg(II) and 1.38 *M* en) in which only the 450-cm⁻¹ Raman line was present. By measuring the intensities of these two lines in these two solutions (using the nitrate peak at 1050 cm⁻¹ as the internal standard) the molar scattering coefficients for the two lines were determined. Then, by measuring the intensities of the two lines, in solutions of intermediate concentrations (0.973 *M* Hg(II) + 7.24 *M* en and 0.730 *M* Hg(II) + 5.43 *M* en) the association constant for the reaction



was evaluated as the average of two determinations. The value came out to be $K_{\text{assoc}} = 0.3$. Because of the low concentrations of the solutions in which dissociation occurred, we were not able to measure the corresponding values for the zinc and cadmium solutions although the frequencies of the bis complexes were detectable. It was found that about equal Raman intensities for tris and bis complexes could be formed only on dilution of the solutions to 0.1 *M* formal concentrations of Zn(II) or Cd(II) and 0.3 *M* en. In such solutions, Raman lines are too weak for quantitative measurement. However, the stability constants indicate that this is, in fact, the concentration where tris and bis complexes should occur in equal amounts, thus confirming our assignments to chemical species.

On dilution, no major changes occurred in the spectrum of the coordinated ligand. Acidification of the zinc-ethylenediamine complex solution completely dissociated the bis complex yielding the (en)H₂²⁺ ion.

Even though the formation constants for the metal-ethylenediamine complexes follow the order Hg > Zn \simeq Cd, the metal-nitrogen stretching frequencies in solution are Hg \simeq Zn > Cd. Probably the larger size of the Cd²⁺ and Hg²⁺ ions has some effect in determining the M-N stretching frequencies. In any case, a similar trend is found for the metal-nitrogen stretching frequencies of the tetraammine complexes of Zn²⁺, Cd²⁺, and Hg²⁺: 427, 350, and 410 cm⁻¹, respectively.⁹ The corresponding values for the bisethylenediamine complexes of Zn²⁺, Cd²⁺, and Hg²⁺ are 450, 435, and 450 cm⁻¹, respectively. The increase in

metal-nitrogen stretching frequencies for each case indicates stronger metal-nitrogen binding on chelation.

Mathieu⁶ has studied the Raman spectra of tris-ethylenediamine complexes of some metals, one of which was zinc. He studied the spectra by preparing the solid tris complexes and dissolving them in water under conditions where some dissociation would be expected. However, his spectra were not complete, and some of the Raman lines reported by him could not be reproduced by us. He has noted that in his solutions some precipitation occurred.

Solid Complexes.—The trisethylenediamine-metal complex ions are expected to have the symmetry D₃. For this point group, vibrations in the species A₁ and E are Raman active, and those in species A₂ and E are infrared active. The A₁ species contains a C-C, a C-N, and an M-N stretching frequency each and two chelate ring deformation vibrations (ignoring the hydrogen vibration frequencies). Species A₂ contains one C-N and one M-N stretching vibration and two ring deformation vibrations. Species E contains a C-C, two C-N, and two M-N stretching vibrations and four chelate ring deformation vibrations.

If one now compares the infrared and Raman spectra of the trisethylenediamine complexes of the three metals given in Table II, it is seen that the strong Raman lines at 420, 408, and 410 cm⁻¹ for zinc, cadmium, and mercury salts, respectively, have no corresponding infrared absorptions. Similarly, the strong infrared absorptions around 500 cm⁻¹ in these compounds have no corresponding Raman lines. On the other hand, near 490, 380, and 280 cm⁻¹, both the infrared and Raman spectra of the complexes have coincident lines. This is the situation one expects for molecules with the point group D₃. A similar situation is found when one considers the 800–1100-cm⁻¹ region for the Zn and Hg complexes. Thus, the strong Raman line at 875 cm⁻¹ for the Zn complex is very weak in the infrared, and that at 872 cm⁻¹ for the Hg complex is absent from the infrared. The lines near 1100 cm⁻¹ (polarized in solution where such measurements are possible) also appear in the infrared. However, as the deuterium experiments indicate, this band is composed of two lines, one the A₁ C-N stretching and the other a coincident NH₂ (E) mode. The latter should persist in the infrared. However, for the solid Cd complex, the situation is not as clear. The 865-cm⁻¹ Raman line is apparently present in the infrared. Although the infrared line might be due to a CH₂ mode,³ it is also possible that in the crystal, Cd(en)₃²⁺ does not have strict D₃ symmetry. It might be noted that for all three complexes the N-H frequencies are relatively low, indicating strong hydrogen bonding possibly either to the anion or to the water of hydration.

For Zn(en)Cl₂, the Raman spectrum has a strong line at 283 cm⁻¹ and the infrared spectrum has two strong absorptions at 285 and 315 cm⁻¹ corresponding to Zn-Cl stretching vibrations. In the Raman spectrum, there are no lines in the 400-cm⁻¹ region, but the infrared spectrum contains three medium-intensity ab-

(9) R. A. Plane, Proceedings of the 8th International Conference on Coordination Chemistry, Vienna, 1964, p 17.

sorptions. The infrared spectrum of this solid is different from those of the solid tris complexes. When the Raman and infrared spectra are compared, it is seen that the stronger infrared absorptions either correspond to weak Raman lines or are absent in the Raman spectra. Conversely, the Raman frequencies are weak or else absent in the infrared. Newman and Powell¹⁰ from an infrared study concluded that this compound consists of Zn atoms bridged by ethylenediamine ligands (each with its two N atoms *trans* to

the C-C bond). Our observation of lack of Raman-infrared coincidence for the ligand frequencies confirm their conclusions. The observation of two Zn-Cl stretching vibrational frequencies (one of them active in both infrared and Raman spectra) rules out the formulation $(\text{Zn}(\text{en})_2)\text{ZnCl}_4$. The Zn-N stretching frequency for this complex may correspond to one of the three infrared absorptions in the 400-cm^{-1} region. Another possibility, which seems to be more likely is that this frequency may be much lower, below the 260-cm^{-1} limit of our spectra. Then, the above three lines would be due to skeletal bending vibrations.

(10) G. Newman and D. B. Powell, *J. Chem. Soc.*, 477 (1961).

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Deprotonation of Tris(ethylenediamine)osmium Halides

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It has been demonstrated that tris(ethylenediamine)osmium(III) iodide can be deprotonated with amide ion or potassium in liquid ammonia or hydroxyl or ethoxyl ions in ethanol. Study of the infrared spectra of the resulting and related species shows that $\nu(\text{NH})$ and $\delta(\text{NH})$ are only little influenced by change in the oxidation state of the central metal ion.

Deprotonation of ethylenediamine ligands associated with transitional metal ions has been effected in one instance in aqueous solution,¹ anhydrous ethylenediamine,² potassium in liquid ammonia,^{3,4} and in numerous cases with amide ion in liquid ammonia,⁵ including also the deprotonation of diethylenetriamine. Since Dwyer and Hogarth² had demonstrated the deprotonation of ethylenediamine complexes of osmium, it was of interest to study deprotonation reactions employing other bases and to determine the effect of changes in the oxidation state of osmium upon properties of the deprotonated species. The results are reported here.

Experimental Section

Methods.—Reactions in liquid ammonia and procedures for handling the products thereof were the same as described elsewhere.⁶ For reactions in ethanol at room temperature, the same equipment was used; ethanol stored over CaH_2 was distilled directly into the reactors cooled with Dry Ice–2-propanol. Air-sensitive products were stored and/or transferred in a drybox containing a He atmosphere maintained oxygen- and water-free by continuous exposure to liquid Na–K alloy.

X-Ray diffraction data were obtained using $\text{Cu K}\alpha$ radiation (Ni filter) at 35 kv and 15 ma and exposure times of 8–20 hr; relative intensities were estimated visually. For the complexes

for which data were not already available, d spacings corresponding to the six most intense lines are given in Table I.

Infrared spectra for Nujol and high-boiling perfluorokerosene (PFK) mulls were recorded with a Beckman IR-7 spectrophotometer with NaCl and CsI interchanges. Data for the $600\text{--}3400\text{ cm}^{-1}$ region are given in Table II and Figure 1 and for the $250\text{--}700\text{ cm}^{-1}$ region in Table III and Figure 2.

Magnetic susceptibilities were determined at 25° with a Curie-Cheneveau balance calibrated against $\text{HgCo}(\text{SCN})_4$; the data were corrected for diamagnetic contributions.

The pK_a value was determined (with an estimated accuracy of $\pm 0.03\text{ pK}_a$ unit) with a Beckman Model G pH meter calibrated against commercial pH 4.10 and 7.00 buffer solutions. The pK_a value was determined from a titration midpoint for a titration of a 1 mM solution of complex with a 0.01 *N* HNO_3 solution; except for employment of dilute solutions, ionic strength was not otherwise controlled.

Materials.—Unless otherwise indicated, all chemicals were reagent grade and anhydrous.

Ammonium hexabromoosmate(IV), $(\text{NH}_4)_2\text{OsBr}_6$, was prepared as described by Dwyer and Gibson.⁷

β -Aminoethylamidobis(ethylenediamine)osmium(IV) iodide,⁸ $[\text{Os}(\text{en-H})(\text{en})_2]\text{I}_3$; bis(β -aminoethylamido)ethylenediamineosmium(IV) iodide and bromide, $[\text{Os}(\text{en-H})_2(\text{en})]\text{X}_2$; and tris(ethylenediamine)osmium(III) iodide dihydrate were prepared by the methods of Dwyer and Hogarth.² *Anal.*⁹ Calcd for $[\text{Os}(\text{en-H})(\text{en})_2]\text{I}_3$: Os, 25.4. Found: Os, 25.6. Calcd for $[\text{Os}(\text{en-H})(\text{en})_2]\text{Br}_3$: Os, 31.2. Found: Os, 31.0. Calcd for $[\text{Os}(\text{en-H})_2(\text{en})]\text{I}_2$: Os, 30.6; N, 13.5. Found: Os, 30.5; N, 13.5. Calcd for $[\text{Os}(\text{en})_3]\text{I}_3 \cdot 2\text{H}_2\text{O}$: Os, 24.2; N, 10.7. Found: Os, 24.3; N, 10.8. The dihydrate (0.6825 g) was dehydrated by

(1) B. P. Block and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **73**, 4722 (1951).

(2) F. P. Dwyer and J. W. Hogarth, *ibid.*, **75**, 1008 (1953).

(3) G. W. Watt, R. E. McCarley, and J. W. Dawes, *ibid.*, **79**, 5163 (1957).

(4) G. W. Watt, L. E. Sharif, and E. P. Helvenston, *Inorg. Chem.*, **1**, 6 (1962).

(5) G. W. Watt and B. J. McCormick, *ibid.*, **4**, 143 (1965), and references therein.

(6) G. W. Watt, *et al.*, *J. Inorg. Nucl. Chem.*, **9**, 311 (1959); *J. Electrochem. Soc.*, **98**, 1 (1951); **102**, 454 (1955).

(7) F. P. Dwyer and N. A. Gibson, *Nature*, **165**, 1012 (1950).

(8) (en- x H) denotes an en ligand from which x protons have been removed.

(9) Analyses were performed as described elsewhere [G. W. Watt and J. T. Summers, *J. Am. Chem. Soc.*, **88**, 431 (1966)] except that the micro Dumas method gave erratic results in the analysis of $[\text{Os}(\text{en-H})_2]$.