TABLE VII

VIBRATIONAL SPECTRA (cm^{-1}) AT 70–400 CM^{-1} FOR SOME TETRAHEDRAL IMIDAZOLE COMPLEXES

		ν(M–L)	ν(M–X)	Other bands
CoL_2Cl_2	Ir	274 mw, 242 w	321 s, 308 s	196 mw, 165 s, 153 sh, 122 m, 105 sh
CoL_2Br_2	Ir	(284 mw, 260 s, 255 sh)[a]		193 s,[b] 183 m, 165 w, 155 m
CoL_2I_2	Ir	283 w, 252 m	237 ms	182 ms,[b] 168 mw, 148 m
ZnL_2Cl_2	Ir	251 mw, 236 w	300 vs, 288 vs	199 ms, 160 m, br, 124 m, 102 w
	R	250 w, 239 m	296 vs, 286 w	216 w, 198 m, 177 w, 159 s, 105 s
ZnL_2Br_2	Ir	(255 sh, 242 vs, 224 mw)[a]		190 s,[b] 158 m, 150 m, 111 w
	R			189 s,[b] 157 w
ZnL_2I_2	Ir	251 m, 232 m	210 s	180 m,[b] 169 m, 148 mw
	R			178 w,[b] 166 m, 145 vs

[a] Bands in parentheses are considered to be due to strongly coupled ν(M–L) and ν(M–X) modes. [b] Possibly a component of ν(M–X).

zinc analog are very similar. This similarity does not, however, extend to the results in the low-frequency region (Table VIII).

TABLE VIII

VIBRATIONAL SPECTRA (cm^{-1}) AT 70–350 CM^{-1} FOR $ML_2(NO_3)_2$ (M = Co, Cu, Zn)

$CoL_2(NO_3)_2$	Ir	323 vs, 298 m, 278 s, 236 sh, 188 sh, 174 s, 145 m, br, 98 m, br
$CuL_2(NO_3)_2$	Ir	330 s, 296 s, 246 w, 233 sh, 222 s, 203 ms, 146 m, 133 m, 103 m
$ZnL_2(NO_3)_2$	Ir	288 s, 250 m, br, 188 w, 169 ms, 144 ms, 131 m, 100 w
	R	245 m, 190 sh, 172 s

The bands observed between 200 and 350 cm^{-1} almost certainly arise from ν(M–L) and ν(M–O) modes. It is likely that metal–oxygen stretching vibrations contribute appreciably to the highest energy bands, but there will be extensive coupling, and attempts at formal assignments to any particular, idealized mode seem unjustified.

Acknowledgments.—We thank the Science and the Agricultural Research Councils for financial support, Miss K. A. Price for preliminary preparative work on some of the compounds, Dr. P. J. Hendra (Southampton University) for some preliminary Raman spectra, and Dr. M. J. Weeks for samples of Ni(imidazole)X_2 (X = Cl or Br). P. J. H. acknowledges the receipt of an S.R.C. Research Studentship.

Notes

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Methylation of Deprotonated Ethylenediamine Complexes of Platinum(II) and Palladium(II)[1]

BY GEORGE W. WATT AND DANIEL H. CARTER

Received May 24, 1968

It has recently been demonstrated[2] that the acidity of the en ligand in $[Pt(bipy)(en)]I_2$ is markedly enhanced by the presence of the associated bipy ligand. Thus $Pt(bipy)(en)^{2+}$ is deprotonated by liquid ammonia while $[Pt(en)_2]I_2$ requires the more strongly basic amide ion.[3] Methylation of the deprotonation products of $Pt(bipy)(en)^{2+}$ served to establish the sites of the successive deprotonations.[2] This work brought into question the possible effect of the bipy ligand upon the reactivity of the deprotonated species in the methylation reaction, particularly since earlier efforts[4] to methylate $Pt(en)(en\text{-}H)^{2+}$ were unsuccessful. Accordingly it was of interest to reexamine the methylation of deprotonated species derived from $Pt(en)_2^{2+}$ and the analogous palladium(II) complexes which are known[5] to differ from the corresponding platinum(II) complexes with regard to both stability and reactivity.

The results given below show that both [Pt(en-H)(en)]I and [Pd(en-H)(en)]I are methylated with methyl iodide under very mild conditions. It must therefore be concluded that an associated π-bonding ligand such as bipy is not a major determinant in the occurrence of the methylation process *per se*.

With reference to the identity of the isomer formed upon methylation of doubly deprotonated $[Pd(en)_2]I_2$, $[Pd(udmen)(en)]I_2$ is eliminated because of its instability when exposed to the atmosphere; $[Pd(men)_2]I_2$ is also eliminated because of lack of correspondence of X-ray diffraction and infrared spectral data (Figure 1) for the two products. The same kinds of data, however, show that the methylation product is $[Pd(sdmen)(en)]I_2$; this conclusion also removes from consideration the removal of one proton from each en ligand in either the *cis* or *trans* positions.

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[1] Abbreviations: en, ethylenediamine; en-*x*H, an en ligand from which *x* protons have been removed; men, N-methylethylenediamine; dmen, a dimethylethylenediamine complex with the position of the methyl groups unspecified; sdmen, N,N′-dimethylethylenediamine; udmen, N,N-dimethylethylenediamine; bipy, 2,2′-bipyridyl.

[2] G. W. Watt and D. G. Upchurch, *J. Am. Chem. Soc.*, **90**, 914 (1968).

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[4] G. W. Watt, unpublished work.

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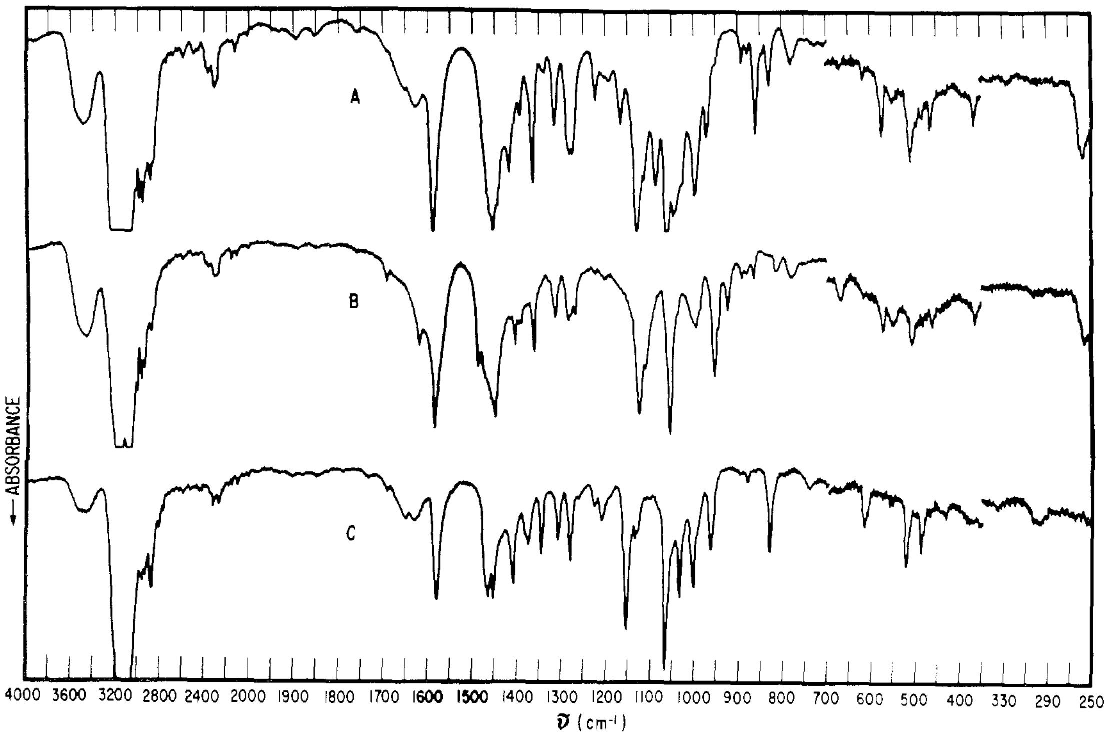

Figure 1.—The infrared spectra of (A) [Pd(sdmen)(en)]I_2 from direct synthesis, (B) [Pd(sdmen)(en)]I_2 from methylation of [Pd(en-2H)(en)], and (C) [Pd(men)$_2$]I_2.

Experimental Section

Materials and Methods.—All experimental procedures, including syntheses, were the same as those described previously.[2,5,6]

Methylation of β-Aminoethylamido(ethylenediamine)platinum(II) Iodide.—About 20 ml of dry CH_3I was distilled under reduced pressure into a reactor containing 0.5 g of [Pt(en-H)(en)]I and a magnetic stirring bar. After stirring for 2 hr at 25°, excess CH_3I was removed by filtration and the pale yellow solid residue was dried *in vacuo* over $Mg(ClO_4)_2$ for 8 hr. *Anal.* Calcd for [Pt(men)(en)]I_2: Pt, 33.4; C, 10.3; H, 3.09. Found: Pt, 33.1; C, 10.6; H, 3.35. X-Ray diffraction data: 4.44 (0.3), 4.21 (1.0), 3.69 (0.5), 3.24 (0.3), 2.86 (0.4). In this and all other cases reported in this paper, incorporation of the methyl group was confirmed by infrared spectral data[7] not recorded here.

Methylation of β-Aminoethylamido(ethylenediamine)palladium(II) Iodide.—This methylation was carried out as described above except that the reaction time was 18 hr; the color of the solid changed from yellow to yellow-brown. *Anal.* Calcd for [Pd(men)(en)]I_2: Pd, 21.5; C, 12.1; H, 3.64. Found: Pd, 21.1; C, 12.1; H, 3.60. X-Ray diffraction data: 4.21 (1.0), 3.95 (0.4), 3.77 (0.4), 3.22 (0.3). This product is stable in dry air but decomposes slowly when exposed to the atmosphere. In dry oxygen-free helium the color changes from yellow to gray in 24 hr but the gray solid gave the same elemental analysis, X-ray diffraction pattern, and infrared spectrum as the original yellow solid; extensive decomposition in helium occurred over 2 days.

In order to establish unequivocally that methylation did indeed generate the men ligand, [Pd(men)(en)]I_2 was synthesized independently by stirring 1 g of Pd(en)I_2 with 0.15 ml of men in 50 ml of water for 3 days at 25°. After removal of unreacted Pd(en)I_2 by filtration, the filtrate was evaporated to dryness at 80° under reduced pressure. The resulting black solid was dissolved in the minimum amount of water and the yellow product was precipitated by addition of 25 ml of ethanol, evaporation to 10 ml, and addition of 50 ml of diethyl ether. The product was filtered and dried *in vacuo* over $Mg(ClO_4)_2$. *Anal.* Calcd for [Pd(men)(en)]I_2: Pd, 21.5; C, 12.1; H, 3.64. Found: Pd, 21.8; C, 12.3; H, 3.80. The infrared spectrum and X-ray diffraction pattern for this compound were virtually identical with those for the product of methylation of [Pd(en-H)(en)]I.

Methylation of [Pd(en-H)$_2$] or [Pd(en-2H)(en)].—Owing to the instability of this complex, it was necessary to effect deprotonation, remove the solvent ammonia, and methylate in the same reactor. Otherwise, the procedure was as above; the reaction time was 4 hr. *Anal.* Calcd for [Pd(men)$_2$]$_2$ or [Pd(dmen)(en)]I_2: Pd, 21.0; C, 14.2; H, 3.94. Found: Pd, 21.0; C, 13.6; H, 3.62. X-Ray diffraction data: 4.87 (0.8), 4.21 (0.2), 3.93 (1.0), 3.69 (0.5), 3.00 (0.5).

Synthesis of Possible Methylation Products.—Since the sites of deprotonation and methylation remained unestablished, it was necessary to synthesize possible isomers; this was done as follows.

Bis(N-methylethylenediamine)palladium(II) iodide, [Pd(men)$_2$]I_2, was prepared by heating 0.5 g of $PdI_2 \cdot H_2O$ and 5 ml of men in 50 ml of water on a steam bath for 1 hr. Unreacted $PdI_2 \cdot H_2O$ was removed by filtration, the yellow filtrate was evaporated to 10 ml, and the product was separated by addition of 50 ml of ethanol. The yellow product was filtered and dried over $Mg(ClO_4)_2$ for 12 hr at 25°. *Anal.* Calcd for [Pd(men)$_2$]I_2: Pd, 21.0; C, 14.2; H, 3.94. Found: Pd, 20.7; C, 14.5; H, 4.05. X-Ray diffraction data: 5.53 (0.5), 4.53 (0.5), 4.25 (0.8), 4.15 (0.5), 4.02 (0.5), 3.74 (0.5), 3.34 (0.8), 3.21 (1.0), 2.76 (0.5).

N,N′-Dimethylethylenediamine(ethylenediamine)palladium(II) iodide, [Pd(sdmen)(en)]I_2, was formed by stirring 1 g of Pd(en)I_2 with *ca.* 0.05 ml of sdmen in 50 ml of water for 2 days at 25°. Otherwise the procedure was the same as for [Pd(men)$_2$]I_2. *Anal.* Calcd for [Pd(sdmen)(en)]I_2: Pd, 21.0; C, 14.2; H, 3.94. Found: Pd, 21.5; C, 13.8; H, 4.00. X-Ray diffraction data: 4.84 (0.4), 4.21 (0.7), 3.93 (0.7), 3.69 (1.0), 3.02 (0.2).[8]

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[7] D. H. Carter, Dissertation, The University of Texas at Austin, 1967.

[8] The product of this synthesis contained small but detectable quantities of [Pd(sdmen)$_2$]I_2 and [Pd(en)$_2$]I_2 impurities not readily removable by recrystallization. Accordingly, [Pd(sdmen)$_2$]I_2 was prepared independently[7] from PdI_2 and sdmen. Examination of the infrared spectra of [Pd(sdmen)$_2$]I_2 and [Pd(en)$_2$]I_2 showed that the bands that are present in Figure 1B but absent in Figure 1A are attributable to these impurities.

N,N-Dimethylethylenediamine(ethylenediamine)palladium(II) iodide, [Pd(udmen)(en)]I_2, was presumably produced by the reaction between 1 g of Pd(en)I_2 and 3 drops of udmen in 50 ml of water as described above. When, however, the pale yellow solid product was filtered and exposed to air, it decomposed to form a hard resinous black solid which could not be characterized.

Acknowledgment.—This work was supported by the Robert A. Welch Foundation and the U. S. Atomic Energy Commission.

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Cobalt(III) Complexes of β-Aminoethyliminodiacetic Acid

BY MARILYN W. S. CHU, DEAN W. COOKE, AND CHUI FAN LIU

Received December 20, 1967

Complexes of various branched-chain tetradentate ligands in which the chain is bifurcated at a donor atom such as β,β′,β″-triaminotriethylamine[1-3] and nitrilotriacetic acid[4,5] have been made and their stereochemistries were studied. However, chelates of this type containing nonidentical arms have never been made before. In the present investigation complexes of one such ligand, β-aminoethyliminodiacetic acid (H_2AEIDA), have been prepared with cobalt(III) and ethylenediamine. Two geometric isomers designated *cis* or *trans*, according to the position of the acetic acid chains with respect to each other, are possible and these have been separated and characterized by essentially the same methods used by Legg and Cooke.[6]

Experimental Section

Preparation of β-Aminoethyliminodiacetic Acid Sulfate ((H_2AEIDA)SO_4).—This ligand was prepared by the method of Schwarzenbach.[7] *Anal.* Calcd for $C_6H_{12}N_2O_4 \cdot H_2SO_4$: C, 26.27; H, 5.14; N, 10.22. Found: C, 25.49; H, 4.66; N, 9.92.

Preparation and Separation of *trans*- and *cis*-(CoAEIDAen)Cl.—(H_2AEIDA)SO_4 (2.1944 g, 8 × 10^{-3} mol) in 20 ml of water was mixed with $Ba(OH)_2 \cdot 8H_2O$ (5.0480 g, 16 × 10^{-3} mol) in 20 ml of water and to the mixture was added carbonatotetramine sulfate[8] (2.0958 g, 4 × 10^{-3} mol) in 70 ml of water. The mixture was heated on a steam bath for 23 hr. After cooling, the barium sulfate precipitate was filtered. To the filtrate was added ethylenediamine dihydrochloride (1.0642 g, 8 × 10^{-3} mol) and the solution was heated on a steam bath for 10 hr. The resulting dark red solution was deposited on a column (diameter 5.5 cm) containing about 400 ml of Dowex 50-WX8 resin (50–100 mesh) in the sodium form. After thoroughly washing with water the column was eluted with 0.5 *N* sodium perchlorate solution at a rate of 1.8 ml/min. Two red bands separated. The large first red band and the small second red band were collected separately. After evaporating to a small volume, these were washed with alcohol and the first band yielded 0.4860 g of the *trans* complex. *Anal.* Calcd for *trans*-(CoAEIDAen)ClO_4: C, 24.47; H, 4.62; N, 14.26; Cl, 9.03. Found: C, 24.42; H, 4.65; N, 14.18; Cl, 8.97.

A portion of the *trans*-(CoAEIDAen)ClO_4 (0.306 g) was converted to the chloride by passing the solution through an anion-exchange column containing Dowex 2-X8 in the chloride form. The complex obtained weighed 0.275 g. *Anal.* Calcd for *trans*-(CoAEIDAen)$Cl \cdot 3H_2O$: C, 25.11; H, 6.32; N, 14.64. Found: C, 25.06; H, 6.23; N, 14.76.

The solution of the second band was evaporated to dryness. The sodium perchlorate was removed by washing with ethanol. Recrystallization of the residue in water gave 0.190 g of the *cis* isomer. Part of the isomer was converted to the chloride in the same way as the *trans* isomer. *Anal.* Calcd for *cis*-(CoAEIDAen)$Cl \cdot 2H_2O$: C, 26.35; H, 6.08; N, 15.26. Found: C, 26.46; H, 6.09; N, 15.49.

Analyses.—The C, H, N, and Cl analyses were done by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

Visible Spectra.—These spectra were recorded at room temperature using a Cary Model 11 spectrophotometer for 10^{-2} *M* solutions in 1-cm cells.

Proton Nuclear Magnetic Resonance Spectra.—These spectra were recorded on a Varian A-60 spectrometer (60 Mc/sec) at about 35°, the internal temperature of the probe. For the *cis* compound a spectrum was also taken on a Varian HA-100 spectrometer (100 Mc/sec) at ambient temperature to get better resolution. D_2O was used as solvent. For the *trans* compound 1 drop of concentrated D_2SO_4 was added to shift the HDO peak downfield about 2 ppm to facilitate the integration of adjacent sample peaks. NaTMS was used as an internal reference.

Results and Discussion

The first band from the column is assigned the *trans* configuration on the basis of visible absorption and proton magnetic resonance spectra. The order of column elution agrees with the results of other investigations on *trans* and *cis* isomers utilizing monodentate ligands[9,10] and on similar CoN_4O_2 systems with multidentate ligands.[6,11]

As summarized in Table I, the two isomers exhibit typical spectra for *trans* and *cis* isomers of this type.[12] In the visible region the *trans* complex shows a shoulder on the high-energy side of the first absorption band while the *cis* isomer exhibits only broadening. The shift in the main peak of the first absorption band from that of the parent compound (using the data for Co-

TABLE I

VISIBLE ABSORPTION SPECTRA[a]

Complex	Spectral bands ($\bar{\nu}$)		
	I_a	I_b	II
trans-(Co(en)-AEIDA)$Cl \cdot 3H_2O$	1.894 (144)[b]	2.237 sh (38)	2.801 (175)
cis-(Co(en)-AEIDA)$Cl \cdot 2H_2O$	1.789 sh (24)[c]	2.008 (107)	2.801 (117)

[a] All $\bar{\nu}$ in $cm^{-1} \times 10^{-4}$. [b] Extinction coefficients (ε) in parentheses. [c] The wavelengths for the shoulders are determined assuming a symmetrically shaped curve for the main peaks.

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