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The Infrared Spectra and Structure of Bis(ethylenediamine)palladium(II) and -platinum(II) Halides[1]

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Received February 9, 1966

Evaluation of the measured spectra for $[M(en)_2]X_2$ ($M^{2+} = Pd^{2+}, Pt^{2+}$, and en = $NH_2CH_2CH_2NH_2$) in relation to an earlier interpretation[2] resulted in several points of disagreement concerning ligand and metal–nitrogen skeletal assignments and the question of hydrogen bonding in the crystalline complexes. Accordingly, the infrared spectra of the complexes $[Pd(en)_2]X_2$ and $[Pt(en)_2]X_2$ ($X^- = Cl^-, Br^-$, and I^-) were reinvestigated to resolve the differences of interpretation; only the chlorides were examined previously.

Experimental Section

Unless otherwise stated all materials used in the syntheses were of reagent grade and were used without further purification. The syntheses of the complexes studied were accomplished by the methods in Table I.[3–6]

Table I

Preparation and Analysis of $[M(en)_2]X_2$ ($M^{2+} = Pd^{2+}, Pt^{2+}$)

Compd	Ref	Pt or Pd	
		Calcd	Found
$[Pd(en)_2]Cl_2$	3	35.7	35.6
$[Pd(en)_2]Br_2$	3	27.5	27.4
$[Pd(en)_2]I_2$	4	22.2	22.0
$[Pt(en)_2]Cl_2$	5	50.5	50.5
$[Pt(en)_2]Br_2$	5	41.1	41.0
$[Pt(en)_2]I_2$	6	34.3	34.2

Deuterated complexes were prepared by dissolving a sample in 99.7% D_2O in a test tube, stoppering the tube, and heating the solution in a water bath at 85–90°. The solvent was removed *in vacuo* over $Mg(ClO_4)_2$. Complete exchange was neither achieved nor strived for as indicated by the resulting spectra. Samples were not analyzed after deuteration.

The unit cell dimensions of $[Pt(en)_2]Cl_2$ have been reported.[7] The complete three-dimensional crystal structural analysis[8] of $[Pd(en)_2]Cl_2$, which is isomorphous with $[Pt(en)_2]Cl_2$, has shown the space group to be $P\bar{1}$. X-Ray powder diffraction data for complexes not previously reported are given in Table II.

Table II

X-Ray Powder Diffraction Data[a]

$[Pd(en)_2]Cl_2$		$[Pd(en)_2]Br_2$		$[Pt(en)_2]Br_2$	
d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0
7.76	1.0	7.81	0.5	7.80	0.8
6.32	0.8	6.51	0.4	6.53	0.6
6.02	0.5	5.25	0.2[b]	6.22	0.3
4.79	0.8	5.02	0.2	4.87	0.3
4.55	0.3[b]	4.70	0.4	4.62	0.6
4.37	0.3	4.58	0.2	4.48	0.4
4.23	0.3	4.30	0.5	4.29	0.7
3.91	0.9	4.04	1.0	4.07	0.5
3.63	0.4	3.76	0.5	3.97	0.9
3.45	0.9	3.54	0.8	3.72	0.6
3.36	0.4	3.48	0.8	3.50	1.0
3.00	0.4	3.10	0.6	3.42	0.2[b]
2.75	0.4	2.80	0.6	3.09	0.5
2.61	0.3	2.49	0.6	2.78	0.5
2.39	0.3			2.44	0.5
2.17	0.3			2.20	0.2
				2.04	0.2

[a] Cu Kα radiation (Ni filter); 35 kv, 15 ma; exposure times, 6–8 hr; relative intensities estimated visually. [b] Less intense lines not included here.

Table III

The Vibrational Assignments for Absorption Bands (cm^{-1}) in the Infrared Spectra of $[Pd(en)_2]X_2$ and $[Pt(en)_2]X_2$

$[Pd(en)_2]X_2$			$[Pt(en)_2]X_2$			Assignment[a]
Cl^-	Br^-	I^-	Cl^-	Br^-	I^-	
3200vs 3075vs	3190vs 3075vs	3180vs 3080vs	3195vs 3140vs 3060vs	3180vs 3155vs 3065vs	3165vs 3060vs	$\nu(NH_2)$
2885vw (?) (?) (?)	2978vw 2958vw 2942vw 2882vw	2970vw 2940vw 2880vw 2845vw	2980vw 2960vw 2945vw 2890vw	2980vw (?) (?) 2890vw	2980vw 2960vw 2880vw 2860vw	$\nu(CH_2)$
1608s 1599s	1595s 1591s	1585s	1613s 1593s	1601s 1583s	1590s	$\delta(NH_2)$
1456s	1454s	1461s 1452s	1457s	1456s	1456s 1450s	$\delta(CH_2)$
1392w 1370s	1392w 1365s	1393w 1363s	1394vw 1374s	(?) 1371m	1393w 1366m	$\omega(CH_2)$
1321m 1136vs	1317m 1131vs	1315m 1125vs	1328m 1163vs	1327m 1158vs	1323m 1154vs	$\omega(NH_2)$
1296m 1277s	1293m 1272s	1288m 1272s	1313m 1279s	1308m 1275m	1302m 1275m	$\gamma(CH_2)$
1127s 999w	1119s 997w	1111s 996w	1140s 1000w	1133s 997w	1127s 993w	$\gamma(NH_2)$
1060s 1052sh	1057vs 1043sh	1056vs	1053s 1045sh	1051s 1040sh	1051s	$\nu(C-N)$
(?)	(?)	1008vw	1026vw	1024vw	1019vw	$\nu(C-C)$
898m 880w	895m 878w	892m 879w	901m 882w	898m 880w	896m 882w	$\rho(CH_2)$
804m	793m	776m	835m	825m	813m	$\rho(NH_2)$
583s 518s	578s 514s	571s 508s	589s 546s	585s 543s	579s 537s	$\nu(M-N)$
473s 374s	469s 369s	463s 364s	479s 363s	475s 360s	469s 355s	$\delta(NCCN)$
290s	272s	255s	290s	276s	264s	$\delta(N-M-N)$

[a] Symbols: ν, stretching; δ, bending (in plane); ω, wagging; γ, twisting; ρ, rocking.

Infrared spectra (Table III and Figure 1)[9] were recorded using a Beckman IR-7 spectrophotometer equipped with NaCl and CsI optics. The compounds listed in Table I were studied as Nujol or hexachloro-1,3-butadiene mulls. The instrument was calibrated with a polystyrene strip in the NaCl region and the rotational spectrum of atmospheric water vapor in the CsI region.

Discussion

The shifts observed in the spectra of $[Pd(en)_2]X_2$ and $[Pt(en)_2]X_2$ can be attributed to cation–anion

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[1] This work was supported by the Robert A. Welch Foundation and the United States Atomic Energy Commission.

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

[3] H. D. K. Drew, F. W. Pinkard, G. H. Preston, and W. Wardlow, *J. Chem. Soc.*, 1895 (1932).

[4] G. W. Watt and R. Layton, *J. Am. Chem. Soc.*, **82**, 4465 (1960).

[5] H. D. K. Drew, *J. Chem. Soc.*, 2328 (1932).

[6] G. W. Watt, R. E. McCarley, and J. W. Dawes, *J. Am. Chem. Soc.*, **79**, 5163 (1957).

[7] G. W. Watt and D. S. Klett, *Acta Cryst.*, **16**, 932 (1963).

[8] E. C. Lingafelter, private communication.

[9] Spectra for the chlorides are shown in ref 2.

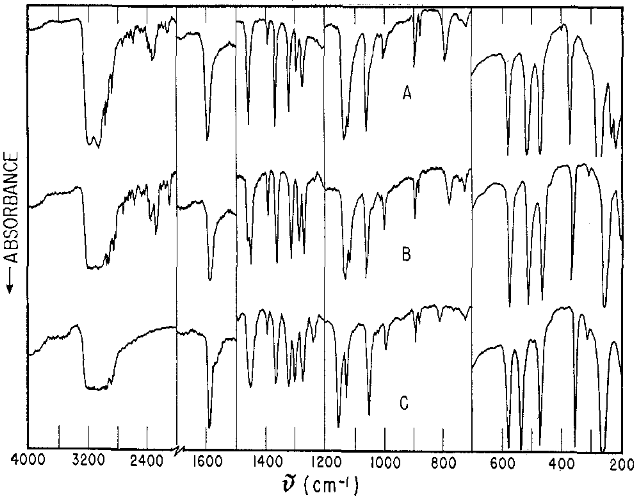

Figure 1.—Infrared spectra of: A, $[Pd(en)_2]Br_2$; B, $[Pd(en)_2]I_2$; C, $[Pt(en)_2]I_2$.

interionic forces, instead of hydrogen bonding between the amino hydrogens and the anion.[2] If the latter effect was important, spectral shifts of the reverse pattern from the observed would be expected. The shifts reported in Table III follow the same trend as observed for $(CH_3)_4NX$ ($X^- = Cl^-, Br^-, I^-$), in which the observed spectral shifts are attributed to electrostatic and repulsive interactions.[10] The data in Table III could also be interpreted in terms of coupling between the unit cell and molecular modes[11] since the I^- lattice would have the lowest absorption frequency.

The crystal structure analysis[8] supports the space group $P\bar{1}$, and with $Z = 1$ requires $[Pd(en)_2]^{2+}$ and $[Pt(en)_2]^{2+}$ to occupy a site of C_i symmetry. The point group C_{2h} contains C_i as a subgroup, whereas the point group D_2 does not.[12] Since the site group and factor group are identical, no correlation field splittings are predicted.[13] Therefore, the applicable selection rules conform to the point group C_i.[14]

The vibrational representation[15] for $[Pd(en)_2]^{2+}$ and $[Pt(en)_2]^{2+}$ assuming C_{2h} symmetry ($\tau_V = 17A_g + 16B_g + 18A_u + 18B_u$) maps into the C_i site group with A_g, $B_g(C_{2h}) \rightarrow A_g(C_i)$ and A_u, $B_u(C_{2h}) \rightarrow A_u(C_i)$. Although not substantiated by Powell and Sheppard,[2] the observation that the complex has a center of inversion does invoke the mutual exclusion rule.[16]

The complete representation for $[M(en)_2]^{2+}$ ($M^{2+} = Pd^{2+}, Pt^{2+}$) can be subdivided among the molecular groups: NH_2 or CH_2 ($6A_g + 6B_g + 6A_u + 6B_u$), N–C–C–N skeleton ($3A_g + 3B_g + 3A_u + 3B_u$), and $M–N_4$ skeleton ($2A_g + B_g + 3A_u + 3B_u$). Since only the *ungerade* modes are infrared active, a total of 36 observable bands is predicted.

The CH_2 motions were found to agree with previous assignments.[2,17] The assignments for all active CH_2 vibrations are listed in Table III.

The assignment of the NH_2 vibrations agreed with Powell and Sheppard[2] as supported by the deuteration studies. As pointed out,[2] the NH_2 rocking motion is apparently moderately coupled to the metal–nitrogen skeletal modes. The NH_2 band assignments are in Table III.

Accordingly, there should be three infrared-active stretching vibrations for the N–C–C–N skeleton: one C–C stretch (A_u) and two C–N stretches ($A_u + B_u$). In crystalline ethylenediamine[18] the C–C stretch has been assigned at 980 cm^{-1} and the C–N stretches at 1065 and 1104 cm^{-1}.

There is a very strong band that appears in the spectrum of each complex between 1050 and 1065 cm^{-1} that shifts slightly on deuteration (*ca.* 6 cm^{-1}). The calculated results of Mizushima, *et al.*,[19] indicate that the molecular transformation from *cis*[18] to *gauche* could cause the two C–N stretches to be nearly accidentally degenerate, while the C–C stretch should remain nearly stationary. The A_u and B_u C–N stretching modes will differ in relative intensity, and, as the anion is varied from I^- to Cl^-, the 1050–1065-cm^{-1} band becomes more unsymmetrical, indicating that a band of lesser intensity is being masked by the stronger peak. Thus, the two C–N stretching modes are assigned to the 1050–1065-cm^{-1} band.

A very weak intensity band is observed in some of the spectra at 1000–1020 cm^{-1} which does not shift on deuteration and is assigned to the A_u C–C stretch. The weak absorption of this mode makes its detection difficult because of the neighboring NH_2 and C–N bands (see Table III).

Powell and Sheppard[2] discussed the metal–nitrogen vibrations only in relation to the stretching modes because their measurements terminated at *ca.* 450 cm^{-1}. They initially discussed the $[Pt(NH_3)_4]^{2+}$ ion in regard to the number of stretching modes expected and the assignment of the data available in the literature. Although not referred to by Powell and Sheppard, Mizushima, *et al.*,[20] discussed this same problem and reported an approximate calculation which concludes that the antisymmetric metal–nitrogen stretching mode should occur at higher frequency than the symmetric stretch, in contrast to Powell and Sheppard.

The $[Pd(en)_2]^{2+}$ or $[Pt(en)_2]^{2+}$ ion should have four metal–nitrogen stretching modes ($A_g + B_g + A_u + B_u$) and five N–M–N deformations ($A_g + A_u + B_u$ for in-plane and $A_u + B_u$ for out-of-plane) under the point group C_{2h}. A schematic representation of the

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(10) G. L. Bottger and A. L. Geddes, *Spectrochim. Acta*, **21**, 1701 (1965).

(11) D. F. Hornig, *J. Chem. Phys.*, **16**, 1063 (1948).

(12) The ethylenediamine ligand assumes a *gauche* configuration [see *e.g.*, A. Nakahara, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, **25**, 331 (1952)]. Thus, across the $[Pd(en)_2]^{2+}$ or $[Pt(en)_2]^{2+}$ complex, the carbons could be either staggered (D_2) or eclipsed (C_{2h}), producing the two possible configurations.

(13) W. Vedder and D. F. Hornig, *Advan. Spectry.*, **2**, 202 (1961).

(14) H. Winston and R. S. Halford, *J. Chem. Phys.*, **17**, 607 (1949).

(15) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, Chapters 5 and 6.

(16) G. W. King, "Spectroscopy and Molecular Structure," Holt, Rinehart, and Winston, Inc., New York, N. Y., 1964, p 366.

(17) I. Nakagawa and S. Mizushima, *Bull. Chem. Soc. Japan*, **28**, 589 (1955).

(18) A. Sabatini and S. Califano, *Spectrochim. Acta*, **16**, 677 (1960).

(19) S. Mizushima, I. Ichishima, I. Nakagawa, and J. V. Quagliano, *J. Phys. Chem.*, **59**, 293 (1955).

(20) S. Mizushima, I. Nakagawa, M. J. Schmelz, C. Curran, and J. V. Quagliano, *Spectrochim. Acta*, **13**, 31 (1958).

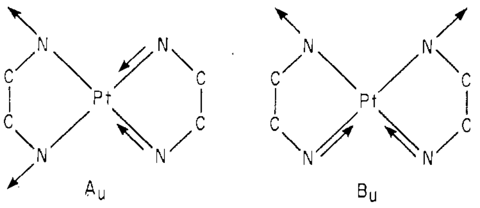

Figure 2.—Schematic drawings of infrared-active metal–nitrogen stretching vibrations.

infrared-active A_u and B_u metal–nitrogen stretching modes is depicted in Figure 2.

Undoubtedly, there is extensive coupling present in the metal–ligand vibrations. For instance, a deformation of N–C–C–N results in the simultaneous deformation of N–M–N. There would be coupling between the M–N stretch and the N–C–C–N deformation. Thus, the observed bands do have a significant degree of mixed character.

The series of six complexes each have two bands in the 500–600-cm^{-1} region that are assigned to the A_u and B_u M–N stretching modes (Figure 1). This assignment is supported by the calculations of Mizushima, *et al.*,[20] and the reported spectrum[21] of $[Pt(NH_3)_4]Cl_2$. Therefore the two infrared-active stretching vibrations are assigned at 571–589 and 508–546 cm^{-1}.

The next two absorption bands that appear in the spectra are assigned to the deformation of the N–C–C–N skeleton. In ethylenediamine[18] the two bending modes of the N–C–C–N skeleton occur at 510 and 468 cm^{-1}. These bands would be frequency dependent on the azimuthal angle between the two N–C–C planes, and hence their absorptions could be significantly shifted in the spectra of the complexes. Poulet, *et al.*,[21] have reported that the deformation of the N–M–N skeleton in $[Pt(NH_3)_4]Cl_2$ occurs below 300 cm^{-1}. Since under the C_{2h} point group two infrared-active N–C–C–N skeletal deformations are predicted ($A_u + B_u$), the two bands in the 355–479-cm^{-1} region are assigned to these vibrations.

The only other band present in the spectra is below 300 cm^{-1}. The broadness of the band suggests that two modes are superimposed and not resolved. The region below 300 cm^{-1} is most certainly the area of poorest resolution in that the instrument slits are at their maximum width. In view of reported data[21] for $[Pt(NH_3)_4]Cl_2$, the 250–300-cm^{-1} band is assigned to the in-plane deformations of the metal–nitrogen skeleton.

The study of Poulet, *et al.*,[21] supports the conclusion that the out-of-plane deformations of the metal–nitrogen skeleton occur below the CsI region.

The N–C–C–N skeleton possesses one infrared-active torsional mode (B_u). In ethylenediamine[11] this torsional motion is assigned at 186 cm^{-1}. Owing to the low frequency that the mode possesses in the uncombined ligand, it is assumed that the band lies below the CsI region in the present complexes.

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Some Spectral Anomalies in Neodymium and Erbium Aminopolycarboxylate Complexes[1]

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Received September 9, 1965

A new series of rare earth chelates with triethylenetetraminehexaacetate (TTHA) ligands has been prepared in solution and their electronic absorption spectra measured. The chelates of Nd^{3+} and Er^{3+} displayed particularly striking intensifications of certain absorption bands, and consequently the analogous chelates with ethylenediaminetetraacetate (EDTA) and *trans*-1,2-diaminocyclohexanetetraacetate (CDTA) ligands were also prepared and their absorption spectra studied, with the hope that some systematic correlation of the spectral enhancements could be made.

Experimental Section

Materials.—Aqueous Nd^{3+} and Er^{3+} solutions (0.1 *M*) were prepared from 99.99% pure chloride salts (Michigan Chemical Corp.). These were standardized by EDTA titration using a xylenol orange indicator. The 0.1 *M* solutions of EDTA and CDTA were prepared by dissolving an accurately weighed required amount of the appropriate acid in 100 ml of water. The 0.1 *M* TTHA (Geigy Chemical Corp.) solution was prepared by dissolving an accurately weighed required amount of the acid in 40 ml of water, to which was added with constant stirring 30 ml of 1.5 *M* NaOH. The solution was then heated to about 80° for 20 min to ensure complete dissolution and made up to 100 ml total volume subsequent to cooling to ambient temperature.

Chelates.—Appropriate volumes of 0.1 *M* rare earth chloride and 0.1 *M* chelon solutions were thoroughly mixed (pH ~8) and set aside for complete equilibration. Maximum spectral enhancements were observed to occur at a 1:1 molar ratio of rare earth ion to ligand in all cases.

Spectral Measurements.—Ultraviolet, visible, and near-infrared absorption spectra were obtained on a Beckman DK-1 recording spectrophotometer. Multiple scans were taken on several samples of each solution to confirm complete accuracy of the results.

Results and Discussion

The observed absorption maxima and ratios of molar extinction coefficients (ϵ_{max}) of complex to aqueous ion of the CDTA, EDTA, and TTHA Nd^{3+} and Er^{3+} chelates are given in Table I. It is observed that, while there is some enhancement in the various ϵ_{max} values for all of the chelates, the most significant effects are found with TTHA ligands, although the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ band in the Nd^{3+}–TTHA system is only about two-thirds as enhanced as that of the $^4I_{15/2} \rightarrow {}^4G_{11/2}$ band of the Er^{3+}–TTHA chelate. Furthermore, a red shift is apparent in this same band where CDTA and EDTA Nd^{3+} chelates are involved, while in the Er^{3+} chelates no shift is discernible except for perhaps a very slight red shift in Er^{3+}–EDTA. It is also interesting that those chelates having ϵ_{max} values significantly enhanced do not

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[21] H. Poulet, P. Delorme, and J. P. Mathieu, *Spectrochim. Acta*, **20**, 1855 (1964).

[1] Presented at the 5th Rare Earth Research Conference, Ames, Iowa, 1965.