lized from chloroform and obtained in red-brown prisms which did not melt below 360°.

Anal. Calcd. for $C_{27}H_{24}O_3N_3Co$: C, 65.2; H, 4.9; N, 8.4; Co, 11.8; mol. wt., 497. Found: C, 64.8; H, 5.0; N, 8.1; Co, 11.8; mol. wt. (Rast, in camphor), 500.

1a,3a,5a-Tris-(α-pyridylmethyleneamino)-cyclohexane Iron(II) Perchlorate (III).—Freshly distilled pyridine-2-aldehyde (2.8 g., 3 moles) was added to a solution of the base I (1.15 g., 1 mole) in ethanol (15 ml.) and the solution refluxed on the water-bath for 5 minutes. The odor of pyridine-2-aldehyde had then disappeared and the color was deep yellow. A solution of iron(II) sulfate heptahydrate (1.3 g., 1 mole) in water (5 ml.) was added, the color at once becoming deep mulberry-red. After addition of perchloric acid (5 ml. of 10%) and cooling the complex iron(II) perchlorate (3 g.) crystallized out. Recrystallized from hot water it formed glistening red plates, m.p. 260° (with violent dec.).

Anal. Calcd. for $C_{24}H_{24}N_6O_8FeCl_2$: C. 44.2; H, 3.7; N, 12.9; Fe, 8.6; mol. wt., 650. Found: C, 44.1; H, 3.9; N, 12.8; Fe, 8.4; mol. wt. (ebullioscopically in water, for ternary electrolyte), 624; mol. cond., 246 mhos.

The compound is diamagnetic.

1a,3a,5a-Tris-(α-pyridylmethyleneamino)-cyclohexanecobalt(II) Perchlorate (IV).—Freshly distilled pyridine-2-aldehyde (2.3 g., 3 moles) was added to a solution of I (1.0 g., 1 mole) in ethanol (10 ml.) and the solution heated gently under reflux for 5 minutes. A solution of cobalt(II) chloride hexahydrate (1.8 g., 1 mole) in ethanol (20 ml.) was then added. The resulting deep blood-red solution was concentrated to small bulk and a solution of perchloric acid (10 ml. of 10%) added. The brownish-pink complex cobalt(II) salt which crystallized was recrystallized from boiling water and obtained in brownish-pink needles, m.p. 280° dec.

Anal. Calcd. for $C_{24}H_{24}N_6O_8Cl_2Co$: C, 44.0; H, 3.7; N, 12.8; Co, 9.0. Found: C, 44.0; H, 3.9; N, 12.6; Co, 8.9.

The compound was paramagnetic with a magnetic moment of 4.73 Bohr magnetons at 22°.

1a,3a,5a-Tris-(α-pyridylmethyleneamino)-cyclohexanecobalt(III) Perchlorate.—The above-described salt IV (0.3 g.) was dissolved in boiling water (20 ml.) and to the solution, carefully cooled so as to avoid crystallization, were added solutions of hydrogen peroxide (5 ml. of 3%) and perchloric acid (5 ml. of 10%). No immediate change in color was discernible. After standing at room temperature for a week the color had changed to mauve and the complex cobalt(III) salt had separated as a violet solid (0.15 g.). It was recrystallized from hot water and obtained in violet plates which did not melt at 300°.

Anal. Calcd. for $C_{24}H_{24}N_6O_{12}Cl_3Co$: C, 38.3; H, 3.2; Co, 7.9. Found: C, 38.6; H, 3.5; Co, 7.8.

The substance is diamagnetic.

1ε,3ε,5ε-Tris-(2′-hydroxy-1′-naphthylmethyleneamino)-cyclohexane Monohydrate.—I (1 g.) was added to a solution of 2-hydroxy-1-naphthaldehyde (2 g.) in ethanol (10 ml.). A deep yellow color developed immediately. After heating at the boiling point for 10 minutes the solution was cooled to 0°. The oil which separated soon solidified after addition of water (1 ml.). Recrystallized from aqueous ethanol it was obtained as a yellow powder, m.p. 165° (with previous softening at 150°).

Anal. Calcd. for $C_{39}H_{33}O_3N_3{\cdot}H_2O$: C, 76.8; H, 5.7; N, 6.9. Found: C, 76.9; H, 5.6; N, 7.1.

1a,3a,5a-Tris-(2′-hydroxy-1′-naphthylmethyleneamino)-cyclohexanecobalt(III) Sesquihydrate.—The method was similar to that used in preparing VII. The substance crystallized from chloroform–methanol in brown microcrystals, m.p. 253°.

Anal. Calcd. for $C_{39}H_{30}N_3O_3Co{\cdot}1^1/_2H_2O$: C, 69.4; H, 4.9; Co, 8.8. Found: C, 69.4; H, 4.7; Co, 8.6.

1a,3a,5a-Tris-(α-pyridylmethyleneamino)-cyclohexanerhodium(III) Perchlorate.—I (0.4 g.) and freshly distilled pyridine-2-aldehyde (0.9 g.) were heated together at 95° for 5 minutes, then rhodium(III) chloride (0.6 g.) was added and the heating continued for 20 minutes. The grey solid which precipitated on addition of dry ether (20 ml.) was collected and dissolved in water (10 ml.). Saturated aqueous sodium perchlorate solution (5 ml.) was added, and the precipitated complex rhodium(III) perchlorate collected and recrystallized from water. It was thus obtained in grey microcrystals.

Anal. Calcd. for $C_{24}H_{24}N_6RhCl_3O_{12}$: C, 36.1; H, 3.0; Rh, 12.9. Found: C, 35.6; H, 3.4; Rh, 12.3.

Acknowledgment.—The authors gratefully acknowledge the assistance of Miss B. Stevenson, who carried out all the C, H and N microanalyses.

SYDNEY, AUSTRALIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Infrared Absorption Spectra of Inorganic Coördination Complexes. X. Studies of Some Metal–Urea Complexes[1a,b]

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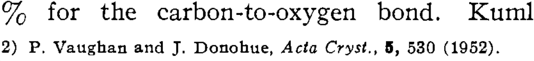
Infrared spectra of some urea–metal complexes have been measured in the 2–35 μ region. From a comparison with the result of the calculation of the normal vibrations of urea, the absorption bands observed in the metal–urea complexes have been assigned. The spectra reveal that urea forms nitrogen-to-metal bonds with Pt(II) and Pd(II), and oxygen-to-metal bonds with Cr(III), Fe(III), Zn(II) and Cu(II).

Introduction

Stable complexes formed from metal salts with 2, 4 or 6 moles of urea are known. However, the inner structures of these complex salts have not been determined.

Vaughan and Donohue[2] considered the structure of urea to involve resonance between the three following structures, the observed values of the interatomic distance indicating 30% double bond



character for the carbon-to-nitrogen bonds leaving 40% for the carbon-to-oxygen bond. Kumler[3]

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(1) (a) Paper IX in series, scheduled to appear March, 1957, in *Spectrochim. Acta*, in press. (b) Abstracted from a portion of the Ph.D. thesis of R. B. Penland, Notre Dame, June, 1956. Presented before the Physical and Inorganic Division of the American Chemical Society, Minneapolis, Minnesota, September, 1955. Supported in part under A.E.C. Contract AT(11-1)-38, Radiation Project of the University of Notre Dame. (c) Visiting Professor, Faculty of Science, Tokyo University.

(2) P. Vaughan and J. Donohue, *Acta Cryst.*, **5**, 530 (1952).

(3) W. D. Kumler and G. M. Fohlen, THIS JOURNAL, **64**, 1944 (1942).

TABLE I[a]

ABSORPTION MAXIMA IN CM.$^{-1}$ OF METAL–UREA COÖRDINATION COMPOUNDS

$[Pd(NH_2CONH_2)_2Cl_2]$	$[Pt(NH_2CONH_2)_2Cl_2]$	$[Cr\{OC(NH_2)_2\}_6]Cl_3$	$[Fe\{OC(NH_2)_2\}_6]Cl_3$	$[Zn\{OC(NH_2)_2\}_2Cl_2]$	$[Cu\{OC(NH_2)_2\}_2Cl_2]$
3390 m	3390 m	3440 s	3440 s	3440 s	3425 s
3290 m	3290 m	3330 s	3340 s	3340 s	3340 s
3140 m	3130 m	3190 m	3190 m	3270 sh	3275 sh
3030 m	3030 m	. . .	. . .	. . .	. . .
1725 s	1725 s	. . .	1655 sh	1660 s	1655 sh
1615 sh	1615 sh	1640 s	1625 s	1640 s	1640 s
1585 m	1590 m	1580 s	1570 s	1630 s	1620 s
. . .	. . .	1555 s	1550 s	1575 s	1580 s
1400 m	1395 m	1505 s	1495 s	1500 sh	1485 s
1145 m	1185 m	1175 m	1170 m	1490 s	1470 s
. . .	. . .	1038 m	1036 m	1145 m	1160 m
910 m	896 m	. . .	. . .	1020 w	1015 w
758 w	757 w	766 m	767 m	776 w	763 m
. . .	. . .	. . .	. . .	765 vw	. . .
. . .	. . .	635 m	615 m	618 w	620 w
585 w	585 w	. . .	. . .	. . .	575 w
535 m	535 m	545 m	540 m	520 m	525 w
438 w	448 w	455 w	. . .	420 w	420 w
338 m	330 m	390 m	330 m	315 w	290 vw

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder.

interpreted the dipole moment of urea as indicating a resonance hybrid with 20–30% contribution of highly polar structures, and considered that the structure of urea is not essentially different from that of simple amides. Resonance of this type in urea is also evidenced by the values of force constants[4] and magnetic susceptibility.[5]

The formation of oxygen-to-metal bonds between urea molecules and the metal ion should bring about only minor changes in many of the urea vibrations. Bellamy and Branch[6] have investigated the spectra of the complexes formed by a number of aldehydes and ketones with metal ions. Coördination, C=O → M, resulted in a shift of the bands in the 6 μ region to lower frequencies. However, the urea molecule may coördinate with metal ions through the nitrogen as well as the oxygen atoms. If a nitrogen-to-metal bond is present in the complex, the spectrum of the complex differs significantly from that of the free urea molecule. The H–N stretching frequencies would be shifted to lower values,[7] and the vibration at about 1700 cm.$^{-1}$ would be shifted to higher frequencies.

The present investigation was undertaken to assign the infrared absorption bands for metal–urea complexes and to determine whether coordination of urea to a central metal ion involves nitrogen or oxygen as the donor atoms.

Experimental

Preparation of Compounds.—Hexa-(urea)-chromium (III) chloride, $[Cr(OC(NH_2)_2)_6]Cl_3$, prepared by the method of Pfeiffer,[8] was recrystallized from hot water as long green needles and dried at 65°.

Anal. Calcd. for $Cr(C_6H_{24}O_6N_{12})Cl_3$: C, 13.89; H, 4.66. Found: C, 13.94; H, 4.72.

Hexa-(urea)-iron(III) chloride, $[Fe\{OC(NH_2)_2\}_6]Cl_3$, prepared by the method of Barbieri,[9] was dried *in vacuo* over phosphorus pentoxide.

Anal. Calcd. for $Fe(C_6H_{24}O_6N_{12})Cl_3$: C, 13.80; H, 4.63. Found: C, 13.89; H, 4.68.

Dichlorobis-(urea)-palladium(II), $[Pd(NH_2CONH_2)_2Cl_2]$, was prepared by the method of Drechsel.[10]

Anal. Calcd. for $Pd(C_2H_8O_2N_4)Cl_2$: C, 8.07; H, 2.71. Found: C, 7.79; H, 2.64.

Dichlorobis-(urea)-platinum(II), $[Pt(NH_2CONH_2)_2Cl_2]$, prepared by a modification of the method of Drechsel,[10] was crystallized *in vacuo* over concentrated sulfuric acid.

Anal. Calcd. for $Pt(C_2H_8O_2N_4)Cl_2$: C, 6.22; H, 2.09. Found: C, 6.16; H, 1.96.

Dichlorobis-(urea)-zinc(II), $[Zn\{OC(NH_2)_2\}_2Cl_2]$, prepared by the procedure of Neubauer and Kerner,[11] was dried over phosphorus pentoxide.

Anal. Calcd. for $Zn(C_2H_8O_2N_4)Cl_2$: C, 9.37; H, 3.14. Found: C, 9.63; H, 3.13.

Dichlorobis-(urea)-copper(II), $(Cu\{OC(NH_2)_2\}_2Cl_2]$, prepared according to the directions of Neubauer and Kerner,[11] was dried at 65°.

Anal. Calcd. for $Cu(C_2H_8O_2N_4)Cl_2$: C, 9.43; H, 3.17. Found: C, 10.16; H, 3.27.

Deuterated compounds were prepared by crystallization of the complexes from D_2O solution.

Absorption Measurements.—All spectra were obtained with a Perkin-Elmer Model 21 recording infrared spectrophotometer employing sodium chloride and cesium bromide prisms over their regions of greatest resolution. The spectra of the solid complexes were obtained by means of the potassium bromide disk technique[12] and checked by measurements in Nujol mulls.

Results

The experimental results obtained for urea complexes are shown in Table I.

Discussion

Yamaguchi and Mizushima[13] have calculated inplane normal vibrations of urea and deuterated urea. From the results of the calculations, the

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[4] L. Kellner, *Proc. Roy. Soc. (London)*, **A177**, 456 (1941).

[5] S. Bhagavantam, *Indian J. Phys.*, **4**, 1 (1929).

[6] L. J. Bellamy and R. F. Branch, *J. Chem. Soc.*, 4491 (1954).

[7] G. F. Svatos, C. Curran and J. V. Quagliano, THIS JOURNAL, **77**, 6159 (1955).

[8] P. Pfeiffer, *Ber.*, **36**, 1927 (1903).

[9] G. A. Barbieri, *Atti accad. naz. Lincei*, **22**, [I] 867 (1913).

[10] E. Drechsel, *J. prakt. Chem.*, [2] **20**, 469 (1879).

[11] K. Neubauer and L. Kerner, *Ann. Chem.*, **101**, 340 (1857).

[12] M. M. Stimson and M. J. O'Donnell, THIS JOURNAL, **74**, 1805 (1952); J. P. Faust and J. V. Quagliano, *ibid.*, **76**, 5346 (1954).

[13] A. Yamaguchi and S. Mizushima, private communication.

assignment of the frequencies observed by them in the region from 500 to 1800 cm.$^{-1}$ is made as shown in Table II.

TABLE II

ABSORPTION MAXIMA IN CM.$^{-1}$ OBSERVED FOR UREA AND DEUTERATED UREA AND THEIR ASSIGNMENTS

	$CO(NH_2)_2$		$CO(ND_2)$	
	Obsd. frequencies	Type of vibration	Obsd. frequencies	Type of vibration
A_1 type	534	δ(NCN)	458	δ(NCN)
	1005	ν(CN)	1001	ν(CN)
	1155	NH_2 rocking	887	ND_2 rocking and ν(CN)
	1603	NH_2 bending and ν(C=O)	1245	ND_2 bending
	1683	ν(C=O) and NH_2 bending	1610	ν(C=O)
B_1 type	601	δ(NCO)	548	δ(NCO)
	1155	NH_2 rocking	887	ND_2 rocking
	1471	ν(CN)	1490	ν(CN)
	1629	NH_2 bending	1245	ND_2 bending

In this calculation the urea molecule has been considered to be planar[14] and to have the symmetry C_{2v}. The Urey–Bradley type of force field was applied. Kellner[4] has also made similar calculations, for a non-planar model, but that made by Yamaguchi and Mizushima is more satisfactory not only in the model but also in the type of force field.

The assignments of the observed frequencies of urea permit the identification of similar vibrations in metal–urea complexes. In the spectra of both dichlorobis-(urea)-palladium(II), $[Pd(NH_2CONH_2)_2Cl_2]$, and dichlorobis-(urea)-platinum(II), $[Pt(NH_2CONH_2)_2Cl_2]$, absorption bands observed at 1725 cm.$^{-1}$, as shown in Fig. 1, can be assigned to the carbonyl vibrations. The presence of a carbonyl vibration at 1725 cm.$^{-1}$ in the spectra of both of these complexes indicates that a coördinate bond is formed between nitrogen and the central metal atom and that oxygen is not a donor atom.

The shift in the 6 μ region of urea is expected to occur upon coördination with metal ions for two reasons: the formation of the $N \rightarrow M$ bond increases the electron demand by the donor nitrogen atom and blocks the resonance between this nitrogen atom and the carbonyl group. Both of these factors bring about increased C=O double bond character.

In addition to the two bands in the 3 μ region similar to those found in the spectrum of urea, attributed to the N–H stretching vibrations, two bands at lower frequencies are observed in the spectra of the Pd(II) and Pt(II) urea complexes (Fig. 1). These are assigned to the N–H stretching vibrations of the coördinated NH_2 group. Since both the free and coördinated N–H frequencies are observed in the spectra of the Pd(II) and Pt(II) urea complexes, it is concluded that only one nitrogen atom of each urea molecule coordinates to the central metal ion. Chemical evidence indicates that the other two coördination positions about the metal atom of the complex are occupied by chlorine atoms.

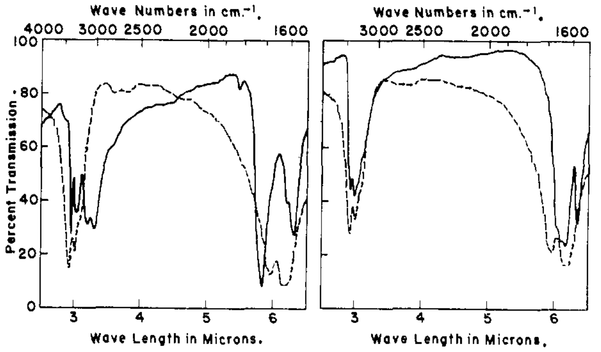
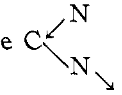
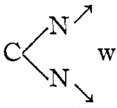


Fig. 1.—(Left) ------, urea, $OC(NH_2)_2$; ——, dichlorobis-(urea)-platinum(II), $[Pt(NH_2CONH_2)_2Cl_2]$; (right) ------, urea, $OC(NH_2)_2$; —— dichlorobis-(urea)-copper(II), $[Cu\{OC(NH_2)_2\}_2Cl_2]$.

As a result of the formation of the nitrogen-to-metal bond, this nitrogen-to-carbon bond acquires more single bond character. This greater C–N single bond character shifts the CN absorption peaks to lower frequencies. The infrared absorption bands at 1395 and 1400 cm.$^{-1}$ in the spectra of $[Pt(NH_2CONH_2)_2Cl_2]$ and $[Pd(NH_2CONH_2)_2Cl_2]$, respectively, which show no isotopic shift on deuteration, can be assigned to a skeletal CN vibration, probably the out of phase 

stretching. Weaker absorption bands at 896 and 910 cm.$^{-1}$ are too low in frequency to be assigned to the corresponding in phase stretching vibration 

which seems to escape detection due to the weak intensity.

From the calculation of the urea vibrations,[13] two types of NH_2 in-plane deformation vibrations are expected. The first type consists of NH_2 bending motions, symmetric and antisymmetric to the axis of symmetry C_2 which are observed in the region about 1600 cm.$^{-1}$. In the case of A_1 type vibrations (*i.e.*, the vibrations symmetric to the C_2 axis and to the plane) the NH_2 bending motions are mixed with the carbonyl vibrations to give the two observed bands at 1683 and 1603 cm.$^{-1}$. The second type of NH_2 deformation vibration consists of symmetric and antisymmetric in-plane rocking motions both observed at about 1155 cm.$^{-1}$.

In the Pd(II) and Pt(II) urea complexes, coordination of one of the nitrogen atoms of each urea molecule to the central metal ion destroys the C_{2v} symmetry of the ligand. Therefore the coupling between various vibrations differs from that in the free urea molecule. Two kinds of NH_2 bending vibrations are expected, one corresponding to the NH_2 group in the free and the other to that in the coördinated part of the urea ligand. From a comparison of frequency values of the free and coordinated urea molecule the bands observed at 1590 and 1585 cm.$^{-1}$ in the spectra of $[Pt(NH_2CONH_2)_2Cl_2]$ and $[Pd(NH_2CONH_2)_2Cl_2]$, respectively, can be considered to arise from the coördinated

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[14] R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **89**, 462 (1934); R. D. Waldron and R. M. Badger, *J. Chem. Phys.*, **18**, 566 (1950).

NH_2 bending vibration. The bands observed as a shoulder at about 1615 cm.$^{-1}$ may be considered to arise from the free NH_2 bending vibration. It was not possible to resolve the peaks associated with the free and coördinated NH_2 rocking vibrations. However, the bands of the Pt(II) and Pd(II) urea complexes observed at 1185 and 1145 cm.$^{-1}$, respectively, may be explained as the free NH_2 rocking or coördinated NH_2 wagging vibrations.[15]

Deformation vibrations of the urea skeleton have been shown by the calculation[13] to occur below about 600 cm.$^{-1}$. From a comparison of frequency values of the free and coördinated urea molecule, the band at 585 cm.$^{-1}$ can be assigned to the δ (NCO) vibration of the coördinated urea ligand and the band at 535 cm.$^{-1}$ to the δ (NCN) vibration. In the case of free urea, the δ (NCO) vibration belongs to the B_1 type of the point group C_{2v}, and the δ (NCN) vibration to the A_1 type, but in the metal complexes as referred to above the C_{2v} symmetry is no longer present.

In accord with chemical evidence,[16] the spectra of both $[Cr\{OC(NH_2)_2\}_6]Cl_3$ and $[Fe\{OC(NH_2)_2\}_6]Cl_3$ indicate that oxygen-to-metal bonds are present in these complexes. The infrared bands observed at 3450 and 3350 cm.$^{-1}$ in the spectrum of urea, assigned to the N–H stretching vibrations, are observed at almost the same frequencies in the spectra of both Cr(III) and Fe(III) urea complexes. An additional less intense band was observed at 3190 cm.$^{-1}$ in the spectra of both of these complexes. The spectrum of urea shows a shoulder very close to this frequency. In many compounds containing NH_2 groups a third NH peak usually of low intensity on the low frequency side is observed in the spectra in the solid state and in electron donor solvents.[17] The spectrum of urea itself taken with lithium fluoride optics indicates the presence of this third N–H band, but it is not clearly resolved.

The bands observed about 1640 cm.$^{-1}$ in the spectra of the Cr(III) and Fe(III) urea complexes can be assigned to NH_2 bending vibrations from a comparison of their frequencies with those of the free urea molecule as well as from the fact that these bands markedly decrease in intensity on deuteration. The formation of the oxygen-to-metal coördination bond in these complexes tends to reduce the coupling between the CO stretching and NH_2 bending vibrations causing them to become more separable. (In the case of the free urea, the NH_2 bending motion is mixed with the CO stretching motion as shown in Table II). The infrared bands observed at 1175 and 1170 cm.$^{-1}$ in the spectra of $[Cr\{OC(NH_2)_2\}_6]Cl_3$ and $[Fe\{OC(NH_2)_2\}_6]Cl_3$ can be assigned similarly to NH_2 rocking vibrations.

As a result of the formation of the oxygen-to-metal bond in the Cr(III) and Fe(III) urea complexes the CO group is no longer at the end of the molecule. Furthermore, coördination increases the single bond character of the CO group, and the CO and CN vibrations are therefore not as separable as in the case of the Pt(II) and Pd(II) urea complexes. The two bands observed at about 1505 and 1038 cm.$^{-1}$ in the spectra of the Cr(III) and Fe(III) urea complexes may be assigned to the CN antisymmetric and symmetric stretching frequencies. Both are higher than the corresponding frequencies of urea. As in the case of the Pt(II) and Pd(II) urea complexes, two frequencies are observed below 650 cm.$^{-1}$ in the spectra of each of the Cr(III) and Fe(III) urea complexes at about 545 and 635 cm.$^{-1}$. These may be assigned to the δ (NCN) and δ (NCO) vibrations, respectively, corresponding to those of free urea observed at 534 and 601 cm.$^{-1}$.

The spectra of Zn(II) and Cu(II) urea complexes (Fig. 1) are quite similar to the spectra of $[Cr\{OC(NH_2)_2\}_6]Cl_3$ and $[Fe\{OC(NH_2)_2\}_6]Cl_3$ discussed above, except that the low intensity band at 3190 cm.$^{-1}$ present in the spectra of the latter two compounds is replaced by a shoulder in the spectra of the Cu(II) and Zn(II) complexes. This similarity reveals the presence of O → M bonds and the absence of N → M bonds in the Cu(II) and Zn(II) complexes. The Pd(II), Pt(II), Cu(II) and Zn(II) complexes all have the same general formula $M(urea)_2Cl_2$ and in each of the first three compounds the chlorine atoms and the donor atoms of the urea molecules are expected to occupy positions at the corner of a square with the metal atom in the center. It is interesting that nitrogen-to-metal bonds are present in the Pd(II) and Pt(II) complexes and oxygen-to-metal bonds in the Cu(II) and Zn(II) complexes.

As explained above many of the infrared bands of the urea complexes in the 3–35 μ region have been assigned. Through this assignment, particularly by the presence or absence of a carbonyl band near 1700 cm.$^{-1}$, and by the presence or absence of shifted NH_2 peaks the urea complexes have been divided into two groups, one with nitrogen, the other with oxygen as the donor atom. This division, suggested by chemical evidence, has been proven conclusively by spectroscopic data.

NOTRE DAME, INDIANA

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(15) S. Mizushima, I. Nakagawa and D. M. Sweeny, *J. Chem. Phys.*, **25**, 1006 (1957).

(16) A. Werner, *Ann. Chem.*, **322**, 302 (1902).

(17) R. J. Dolter, Ph.D. Thesis, University of Notre Dame, 1952.