and has a Br···H(N2) separation of 2.68 Å, but we do not believe that this is a hydrogen bond since Br···N contacts of considerably less than 3.48 Å which do not involve hydrogen bonding are quite common in systems of this type. Thus, there is a Br(2)···N(1) (N(1) is the pyridine nitrogen atom) separation of 3.195 Å in this molecule, and there are Br···N contacts of 3.101 (9) and 3.105 (9) Å in dibromobis(2,3-dimethylpyridine)copper(II).[40]

The Cu-N bond lengths are consistent with those found in related systems. Hence, the Cu–N(1) distance of 2.021 (5) Å is similar to the values of 1.98 (1) and 2.02 (1) Å in dichlorobis(2-methylpyridine)copper(II),[41] 1.989 (6) Å in *trans*-bis[(chloroacetato)(2-methylpyridine)]copper(II),[42] 1.99 Å in dibromobis(pyridine)copper(II),[28] 2.02 Å in dichlorobis(pyridine)copper(II),[43] and 2.161 (10) Å in 2-methylpyridinecopper(II) chloroacetate.[44] Similarly, the Cu–N(2) separation of 1.989 (6) Å is comparable to the values of 1.971 (2) and 1.984 (2) Å in carbonatodiamminecopper(II),[45] 2.012 (9) and 2.017 (9) Å in selenatotetraamminecopper(II),[46] 2.031 (6) and 2.032 (6) Å in sulfatotetraamminecopper(II),[46] and in other copper–amine systems. The pyridine ring is planar, with no atom deviating from the least-squares plane by more than 0.012 Å. The bond lengths and angles in the ring and in the exocyclic aminoethyl group are similar to those found in other pyridine and substituted-pyridine complexes.[41–44]

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CONTRIBUTION FROM THE LOUISIANA STATE UNIVERSITY IN NEW ORLEANS, NEW ORLEANS, LOUISIANA 70122,
AND THE SOUTHERN REGIONAL RESARCH LABORATORY,[1c] NEW ORLEANS, LOUISIANA 70179

The Crystal and Molecular Structure of Hexakis(2-imidazolidinone)cadmium(II) Perchlorate

BY J. N. BROWN,[1a] A. G. PIERCE, JR.,*[1b] AND L. M. TREFONAS[1a]

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The crystal and molecular structure of hexakis(2-imidazolidinone)cadmium(II) perchlorate has been determined by a single-crystal X-ray diffraction study using diffractometer data. The title compound crystallizes in the space group $P\bar{1}$ with one molecule in a unit cell with dimensions $a = 11.298$ (1) Å, $b = 12.299$ (1) Å, $c = 6.377$ (1) Å, $\alpha = 96.20$ (1)°, $\beta = 94.61$ (1)°, and $\gamma = 114.29$ (1)°. The structure was solved by the heavy-atom method and refined by block-diagonal least squares to a final value of the conventional reliability index (R) of 0.046 for the 2364 statistically significant reflections. The ethyleneurea ligands are coordinated through the carbonyl oxygen and form a distorted octahedron about the cadmium with Cd–O distances of 2.348 (5), 2.282 (4), and 2.239 (4) Å and with O–Cd–O angles ranging from 86.1 to 93.9°. An extensive pattern of hydrogen bonding between the amide nitrogens and the carbonyl oxygens of adjacent ethyleneurea groups is observed.

Introduction

The coordination chemistry of ureido compounds has received considerable attention in recent years. Ureas (or any amide-type compound) possess two potential sites for coordination, the carbonyl oxygen and the amide nitrogen. Although Neubauer and Kerner reported the first urea complex in 1857,[2a] it was not until 100 years later that Penland and coworkers[2b] used infrared spectroscopy to predict the mode of bonding (*i.e.*, nitrogen to metal or oxygen to metal) in a series of urea complexes. Since that time, many references in the literature have suggested that the mode of bonding can be deduced from the position of the carbonyl stretching frequency of the complex relative to that of the free ligand.[3–5] A shift of the carbonyl absorption to lower frequency is presumed to indicate oxygen to metal bonding, while a shift to higher frequency would indicate nitrogen to metal bonding. For example, based on infrared spectral data, Penland and coworkers postulated oxygen to metal bonding in urea complexes of Cr(III), Fe(III), Zn(II), and Cu(II) and nitrogen to metal bonding with Pt(II) and Pd(II). Costamagna and Levitus[6] used similar arguments to demonstrate oxygen to metal bonding in a series of cobalt complexes with N-substituted ureas. Madan and Denk[7] correlated

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[1] (a) Louisiana State University in New Orleans. (b) Southern Regional Research Laboratory. (c) One of the laboratories of the Southern Marketing and Nutrition Research Division, Agricultural Research Service, U.S. Department of Agriculture.

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infrared spectra, conductance measurements, and analytical data to indicate oxygen coordination in a series of caprolactam complexes. Berni, Jonassen, and Benerito[8,9] studied complexes of both ethyleneurea and propyleneurea with anhydrous metal chlorides. Their infrared data suggested that the 2:1 complex of ethyleneurea with cadmium chloride might be symmetrically bonded through the π cloud over the entire three-atom amide system.

Amides and their heterocyclic analogs are weak bases, forming, on protonation, cations which are potentially tautomeric. During the past 20 years, the relative importance of O-protonation and N-protonation of amides has received considerable attention in the literature, and much evidence in support of each has been advanced without complete agreement having been reached. The primary argument advanced in favor of N-protonation is the shifting of the carbonyl absorption to higher frequency upon protonation. Since the formation of a coordination complex with amides involves the donation of a pair of electrons from the ligand to a vacant orbital on the central ion, the mechanism is the same regardless of the nature of the central ion (either a metal ion or a hydrogen ion).

A series of structural studies has been undertaken to investigate the validity of this correlation of the shift of the carbonyl stretching frequency to the prediction of the mode of bonding. As part of that study, complexes were synthesized between either 2-imidazolidinone (ethyleneurea, I) or 2-(1*H*)-tetrahydropyrimidinone (propyleneurea, II) and the perchlorate salts of magnesium, calcium, zinc, cadmium, mercury, chromium, iron, nickel, cobalt, and copper. The hexakis(2-imidazolidinone)cadmium(II) perchlorate reported herein was chosen as the initial compound to be investigated because it, unlike most of the others in the present series studied, exhibits no shift of the carbonyl band relative to that of the free ligand.

Experimental Section

The general method of synthesis was that proposed by Madan and Denk.[7] The hydrated cadmium perchlorate (0.01 mol) was dehydrated by stirring for 30 min at room temperature with 2,2-dimethoxypropane (0.08 mol, 33% excess). Ethyleneurea (0.06 mol) dissolved in a minimum of methanol was added to the resulting anhydrous solution, and stirring was continued for an additional 20 min. Diethyl ether was added slowly until the solution became slightly cloudy. The solution was allowed to stand for 16 hr at room temperature during which time slow crystallization took place. The solids were collected by suction filtration, washed twice with ether, and dried under vacuum at 40°. *Anal.* Calcd for $CdC_{18}H_{36}N_{12}O_{14}Cl_2$: C, 26.12; H, 4.38; N, 20.30. Found: C, 26.35; H, 4.30; N, 20.18.

Single crystals suitable for an X-ray diffraction study were grown from methanol. A single, irregularly shaped crystal with a maximum dimension of 0.2 mm was mounted with the (00*l*) axis coincident with the ϕ-axis of a General Electric XRD-5 diffractometer. The reciprocal lattice showed no evidence of mirror or rotation symmetry nor any systematic absences limiting the crystal to a triclinic system and either space group $P1$ or $P\bar{1}$. Consequently, axes which are suitable for a triclinic crystal and which conform to the usual conventions were selected. Lattice constants were then determined by a least-squares fit of 48 carefully measured 2θ values of the Cu $K\alpha_1$ and Cu $K\alpha_2$ doublet for $2\theta > 90°$ under fine conditions (1° takeoff angle and a 0.05° slit). The resultant lattice constants and their estimated standard deviations (esd) are $a = 11.298$ (1) Å, $b = 12.299$ (1) Å, $c = 6.377$ (1) Å, $\alpha = 96.20$ (1)°, $\beta = 94.61$ (1)°, and $\gamma = 114.29$ (1)°.

The calculated density of 1.72 g/cm³ for one molecule per unit cell is consistent with the experimentally measured density of 1.70 ± 0.02 g/cm³ obtained by flotation methods.

Intensity data were collected on a General Electric XRD-490 fully automated diffractometer by the stationary-crystal, stationary-counter method using balanced Zr–Y filters and Mo $K\alpha$ radiation. A total of 2675 reflections were measured to a 2θ maximum of 50° ($d = 0.841$ Å). Of these, 2364 (88%) reflections were considered observed by the criterion $(I_{Zr} - 2\sigma(I_{Zr})) - (I_Y + 2\sigma\ (I_Y)) > 200$ (where the σ's are based entirely on counting statistics). Lorentz–polarization corrections were made in the usual manner and absorption (8% maximum) was corrected as a function of ϕ (polar axis) (linear absorption coefficient $\mu = 9.2\ \text{cm}^{-1}$ for Mo radiation).

Structure Determination

A three-dimensional Patterson function was calculated and used to resolve the ambiguity between $P1$ and $P\bar{1}$. Because only one unique vector of height suitable for a Cd–Cl was found on the map, $P\bar{1}$ was chosen as the space group with the Cd fixed at the origin. The coordinates of the chlorine atom and the isotropic temperature factors of both the cadmium and the chlorine atoms were refined by block-diagonal least squares[10] to a value of $R = 0.37$. An electron density map phased by these atoms revealed all of the lighter atoms of the three unique ethyleneurea groups and the oxygen atoms of the perchlorate group. Weighted, isotropic refinement, using all 24 atoms led to a value of $R = 0.07$. Weights of individual reflections were taken as $1/\sigma^2$, where $\sigma = {}^1/_2\sqrt{Q(1 + B)/(1 - B)}$, Q = f(absorption correction, Lorentz–polarization factor, scaling factor), and $B = I_Y/I_{Zr}$. After conversion to anisotropic temperature factors, refinement was continued until convergence at $R = 0.046$. At this stage, all shifts in coordinates and temperature factors were less than one-tenth the estimated standard deviations of the respective parameters and the refinement was terminated.[11]

Results and Discussion

Table I lists the final coordinates and anisotropic temperature factors for all of the atoms together with the estimated standard deviations (esd's) for all of the parameters. Maximum esd values for the various bond distances are as follows: Cd–O, 0.005 Å; Cl–O, 0.01 Å; light-atom distances, 0.013 Å. In no case is there a bond angle with an esd value greater than 0.7°. Excluding the distances and angles involving the cadmium, all esd values are thus on the order of 0.01 Å in the distances and 0.7° in the angles. Consequently the following comparisons and conclusions will implicitly assume these esd values and the various distances and angles will be discussed without appending their esd values.

The perchlorate group is usually assumed[12] to have tetrahedral symmetry with Cl–O distances in the range of 1.40–1.48 Å. Unfortunately, it is also usually found to be disordered in crystallographic studies[13] and, depending on the manner in which the disordering is handled, a much wider variation in the Cl–O distances combined with O–Cl–O angles ranging from 103–112° are reported. In this study, the perchlorate group does refine as an ordered group with Cl–O distances (1.36 1.40, 1.41, 1.43 Å) which, although covering a wide range, average to 1.40 ± 0.02 Å. The O–Cl–O angles (106.3–111.0°) average to 109.5 ± 1.2°. The short

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[10] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

[11] A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1830. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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TABLE I

FRACTIONAL COORDINATES AND ANISOTROPIC THERMAL PARAMETERS[a]

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cd	0.0000 (0)	0.0000 (0)	0.0000 (0)	56 (1)	41 (1)	147 (2)	14 (1)	−16 (1)	13 (1)
Cl	0.7135 (2)	0.3778 (2)	−0.0417 (3)	130 (3)	61 (2)	334 (7)	21 (2)	−38 (4)	18 (3)
Ox1	0.7837 (8)	0.3412 (8)	0.0941 (15)	214 (13)	291 (14)	1097 (48)	43 (11)	−146 (20)	395 (22)
Ox2	0.7988 (6)	0.4879 (5)	−0.1065 (9)	222 (10)	75 (6)	386 (21)	27 (6)	−31 (12)	41 (9)
Ox3	0.6123 (7)	0.3923 (6)	0.0563 (14)	206 (11)	123 (8)	1078 (46)	51 (8)	160 (19)	54 (16)
Ox4	0.6523 (8)	0.2874 (6)	−0.2176 (12)	330 (15)	134 (9)	605 (32)	5 (9)	−38 (18)	−126 (14)
O-1	0.2059 (4)	0.0456 (4)	−0.1117 (7)	61 (5)	89 (5)	189 (13)	24 (4)	−21 (7)	36 (6)
C1-1	0.2970 (6)	0.0510 (6)	0.0208 (10)	62 (8)	76 (7)	184 (19)	23 (6)	31 (10)	14 (9)
N2-1	0.3093 (6)	−0.0434 (5)	0.0894 (9)	93 (7)	84 (6)	243 (18)	40 (6)	−31 (9)	55 (9)
C3-1	0.4159 (8)	−0.0054 (7)	0.2668 (12)	97 (10)	107 (9)	293 (27)	20 (8)	−64 (13)	37 (12)
C4-1	0.4935 (8)	0.1312 (7)	0.2543 (13)	100 (10)	126 (10)	316 (27)	54 (8)	−49 (13)	14 (13)
N5-1	0.3996 (5)	0.1557 (5)	0.1151 (10)	66 (7)	88 (7)	314 (21)	21 (5)	−49 (10)	−3 (9)
O-2	0.1088 (4)	0.0844 (4)	0.3270 (6)	85 (6)	49 (4)	161 (12)	15 (4)	−27 (7)	12 (6)
C1-2	0.1906 (6)	0.1899 (5)	0.4032 (9)	62 (7)	50 (6)	149 (18)	13 (5)	−19 (9)	10 (8)
N2-2	0.2670 (5)	0.2160 (5)	0.5898 (8)	91 (7)	61 (6)	194 (17)	2 (5)	−53 (9)	13 (8)
C3-2	0.3405 (8)	0.3497 (6)	0.6538 (13)	161 (13)	48 (7)	334 (28)	−13 (7)	−113 (15)	23 (11)
C4-2	0.3166 (8)	0.3979 (7)	0.4447 (13)	140 (12)	62 (8)	336 (28)	−16 (7)	−114 (14)	38 (12)
N5-2	0.2117 (6)	0.2893 (5)	0.3146 (9)	94 (7)	46 (5)	273 (19)	4 (5)	−42 (9)	36 (8)
O-3	0.0259 (4)	0.1850 (4)	−0.0752 (7)	109 (6)	50 (4)	185 (13)	25 (4)	−34 (7)	23 (6)
C1-3	−0.0127 (6)	0.2200 (5)	−0.2355 (10)	73 (8)	46 (6)	191 (19)	22 (6)	0 (10)	17 (8)
N2-3	0.0164 (7)	0.3348 (5)	−0.2499 (9)	176 (10)	52 (6)	278 (20)	39 (6)	−72 (11)	30 (8)
C3-3	−0.0459 (8)	0.3482 (7)	−0.4523 (11)	175 (13)	75 (8)	229 (23)	63 (8)	−32 (14)	25 (11)
C4-3	−0.1157 (7)	0.2149 (6)	−0.5716 (11)	122 (10)	62 (7)	239 (23)	37 (7)	−62 (12)	30 (10)
N5-3	−0.0916 (6)	0.1463 (5)	−0.4117 (8)	117 (8)	61 (5)	165 (16)	34 (5)	−30 (9)	24 (7)

[a] Anisotropic temperature factors of the form $\exp\{-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]\}$. Standard deviations ($\times 10^4$) in parentheses.

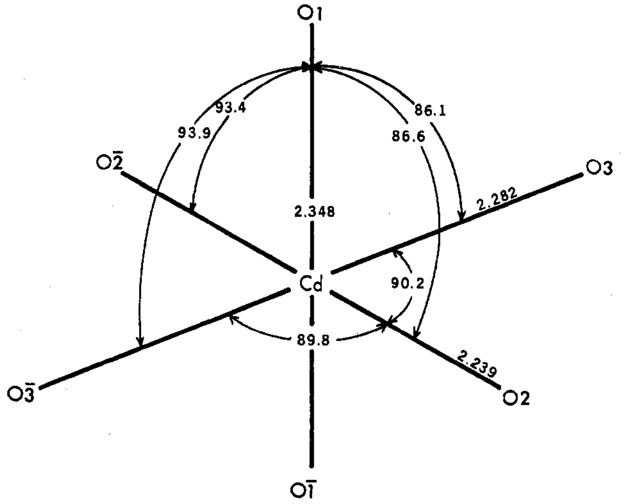

Figure 1.—Schematic drawing of the coordination sphere about the cadmium.

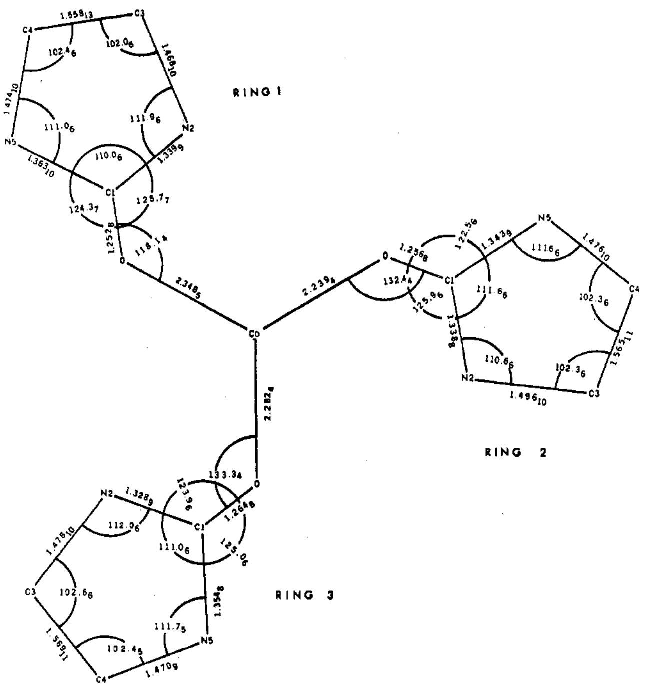

Figure 2.—Schematic drawing of bond distances and angles within the ethyleneurea groups. Lower case numbers are the standard deviations for the calculated parameters.

(2.95 Å) contact distance between the nitrogen of the ethyleneurea (N2-3) and one of the oxygen atoms of the perchlorate group (Ox2) suggests weak hydrogen bonding between the two as the factor allowing the perchlorate group to be observed as an ordered group.

Figure 1 illustrates the local environment of the cadmium atom. The Cd–O distances (2.239, 2.282, 2.348 Å) differ from each other by more than five standard deviations and so should not be averaged. If the oxygens with the two shorter distances, together with the cadmium atom, are used to define the reference plane (as in Figure 1), then they, together with their centrosymmetric equivalents, closely approximate tetragonal symmetry with O–Cd–O angles from 89.8 to 90.2°. The remaining oxygen (Cd–O = 2.348 Å) is then the most distorted feature of the octahedron with angles to the reference plane ranging from 86.1 to 93.9°. This symmetry results primarily from a systematic pattern of hydrogen bonding within the reference plane while the unique ring and its centrosymmetric equivalent have only one short contact distance each of which can be attributed to hydrogen bonding.

The ethyleneurea groups are identical with each other well within their esd values as is evident from the schematic drawing (Figure 2) which lists the bond distances and angles within each of the ligands. If one takes an average value for equivalent bonds over all of the ethyleneurea groups, then the C–O, C–N average distances of 1.257, 1.345 Å, respectively, compare to those cited by Donohue and Post[14,15] for urea. The

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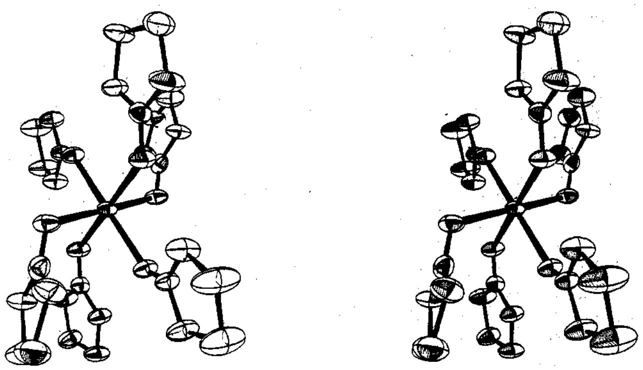

Figure 3.—ORTEP stereo diagram of the cation.

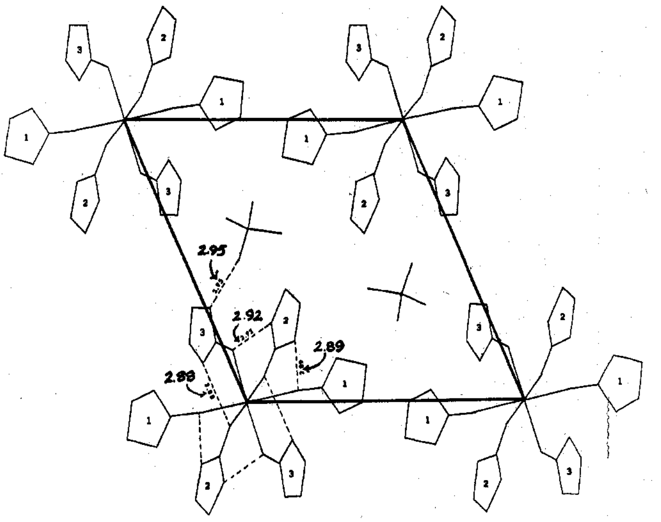

Figure 4.—Projection of the unit cell contents down the (001) axis showing hydrogen-bonding scheme. *a* axis across; *b* axis up.

remaining C–N distance and the average C–C distance (1.478, 1.564 Å, respectively) agree well with the expected values for these distances.[15]

The relatively short N···O contact distances (2.877, 2.914 Å) found alternately between the four ethyleneurea groups (labeled as rings 2, 3 and their centrosymmetric equivalents $\bar{2}$, $\bar{3}$) strongly suggest a pattern of hydrogen bonding. The third ethyleneurea group (labeled as ring 1) has only one such short contact distance (2.894 Å from oxygen O-1 to the nitrogen N2-2) and is, in turn, the ring most distorted from octahedral symmetry with the longest Cd–O distance at 2.348 Å (in Figure 1, this would be the ring indicated by the oxygen not in the reference plane).

Figure 3 gives an ORTEP stereoview of the entire cation including the cadmium and the three unique ethyleneurea ligands together with their centrosymmetric equivalents. Finally, Figure 4 shows the contents of a unit cell with the short N···O contact distances indicative of hydrogen bonding illustrated in the figure.

In this particular compound the carbonyl stretching frequency lies at the same place in the spectrum (1669 cm^{-1}) as it does in free ethyleneurea itself. However, because the compound has Cd–O linkages, spectral shifts to lower frequency for the carbonyl stretching frequency are predicted. The hypothesis obviously fails in this case. Further studies with compounds having shifts to higher and lower frequencies, respectively, are nearing completion. Preliminary results from both of these studies confirm the conclusions of this study. Namely, very little validity can be placed on hypotheses correlating carbonyl stretching frequency shifts to type of bonding (metal to nitrogen *vs.* metal to oxygen bonding). The structure results do suggest one spectral characteristic worthy of mention. Four of the six urea rings lie in the equatorial plane containing four of the C–O–Cd bonds. These rings are, in turn, hydrogen bonded to each other forming an equatorial network. The remaining two rings are axial with a dihedral angle of 100° with this equatorial plane and are not hydrogen bonded. This suggests that there should be two unique Cd–O stretching frequencies corresponding to the equatorial and axial Cd–O bonds.

As mentioned earlier, the mechanism of complex formation is independent of the nature of the central ion (metal or hydrogen). Hence our structural data tend to support the evidence in the literature in favor of oxygen protonation of amides, rather than nitrogen protonation.[16,17]

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[16] *Chem. Soc., Spec. Publ.*, **No. 11** (1958); Supplement (1964).

[17] V. C. Armstrong, D. W. Farlow, and R. B. Moodie, *J. Chem. Soc. B*, 1099 (1968).