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STRUCTURAL AND SPECTROSCOPIC PROPERTIES OF METAL–UREA COMPLEXES

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ABBREVIATIONS

DNA	deoxyribonucleic acid
EPR	electron paramagnetic resonance
IR	infrared
FT–IR	Fourier transform infrared
NMR	nuclear magnetic resonance
NQR	nuclear quadrupole resonance
UV	ultraviolet
M	metal

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A. INTRODUCTION

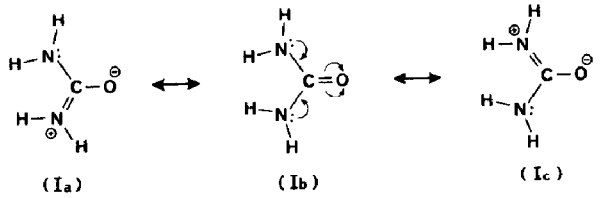
Developments in coordination chemistry and in particular in the stereochemistry of coordination compounds which are biologically important will be exciting during the next half century. The arrangement of atoms in complexes, the coordination numbers, the conformation of the biological molecules once they are attached to the metal, etc. will be topics of considerable importance in particular in medicine and in health sciences. Over the past years certain platinum compounds have been used as anticarcinogenic agents for cancer patients. The compounds impair mitosis of the affected cells by binding between the ellipsoid strands of DNA. Many researchers work with similar compounds on biological models to determine their action and study the interaction of these platinum compounds with specific receptor sites in DNA. In order to study these different systems, researchers use modern techniques, such as, Raman, infrared (IR), X-ray, ^{1}H,^{13}C,^{31}P nuclear magnetic resonance (NMR) spectroscopy, etc. The study of the stereochemistry of the metal complexes of urea is not new, but since the development of instrumental methods, such as X-ray, infrared, Raman ultraviolet absorption and NMR the chemical bonds have been greatly refined and whole new areas of stereochemistry have been opened. For example, we now have a more clear understanding of the crystal structures, the molecular structures and the coordination numbers of metal complexes.

In this review we have attempted a systematic study of the metal–urea compounds. The metal–urea complexes are an interesting group of compounds with which to investigate the metal–oxygen and metal–nitrogen chemical bonds and the effect of metal interaction on the structure and properties of urea. Some of these metal–urea compounds have antimicrobial and antivirial properties and could be effective against diseases. Vitamin B_{12}, an inorganic coordination compound, is rich in $-CONH_2$ groups, which reminds us of the biological importance of urea in the design of complicated molecules in life.

B. PROPOSED STRUCTURES OF UREA

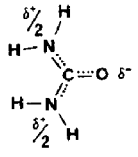
Urea was the first organic substance synthesized in the laboratory, by Wöhler in 1828. Urea ($(NH_2)_2CO$) is a weak base and lacks any acidic property [1]. It is a basic substance and forms salts with acids [2]. Three resonance structures can be written for urea [3] (see scheme 1).

The proposed structures are in qualitative agreement with the resonance energy of 73 kcal mol^{-1} [4,5] calculated for these structures. The two equivalent forms with a charge separation (structures **Ia** and **Ic**) lead to the great stability of urea. The observed values of interatomic distances for urea



(Ia) (Ib) (Ic)

Scheme 1.



(II)

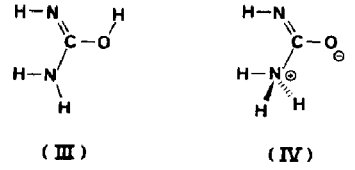
Scheme 2.

[3,6] are C–O, 1.26 ± 0.01 Å; and N–C, 1.34 ± 0.01 Å. These distances indicate 20–30% double bond character for carbon–nitrogen bond and 50–60% for the carbon–oxygen bond [7]. The structures **Ia, Ib** and **Ic** can be resumed as an average structure **II** (see scheme 2).

There is some evidence reported in the literature indicating the hybrid resonance structures of urea. The dipole moment of 4.56 D of urea in dioxane at 25°C indicates a contribution of structure **Ib** with 20–30% of highly polar structures [8,9]. The values of force constants [10] and magnetic susceptibility [11] are also consistent with the presence of resonance in the structure of urea.

In earlier years [12] the possibility of an enolic form (structure **III** and the zwitterionic form (structure **IV**) [13] together with the canonical forms of urea as minor or major components were proposed (see scheme 3). These structures were quickly discarded because they were inconsistent with urea's chemical properties.

For many years, the exact structure of urea was a mystery. Some crystallographic studies on urea were undertaken [6,14,15], but were not sufficiently accurate to determine the exact structure. Vaughan and Donohue [3]



(III) (IV)

Scheme 3.

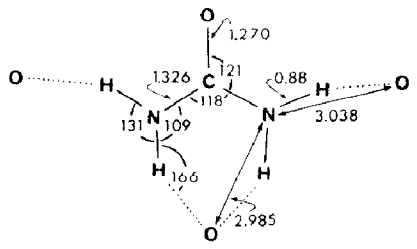
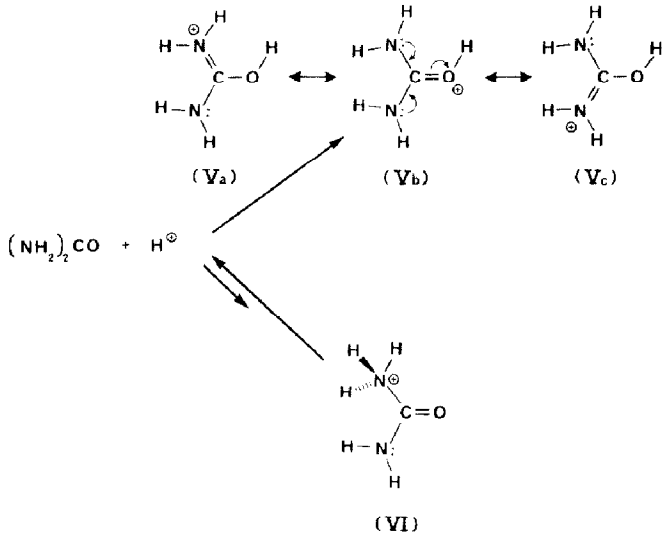


Fig. 1. View of urea structure showing bond distances (Å) and angles (°). Hydrogen bonds are indicated by broken lines, adapted from ref. 21.

determined the precise oxygen, nitrogen and carbon parameters and obtained a good indication of the hydrogen atoms coplanar to the rest of the molecule. Previous infrared [16,17], NMR [18,19] and later neutron diffraction studies [20] led to similar conclusions.

Several years later, Caron and Donohue [21] corrected the dimensional least squares refinement of urea [3], and submitted the revised values of interatomic distances and bond angles shown in Fig. 1. Figure 1 shows the urea molecule and its bond distances and bond angles. The negatively charged oxygen atom from structures **Ia** and **Ic** is capable of coordinating with one proton. It acts as a monobasic substance and forms salts with acids [2]. In a 1 : 1 addition of an acid with urea in aqueous solutions adducts are formed with the following formulae: $(NH_2)_2CO \cdot HCl$, $(NH_2)_2CO \cdot H_2SO_4$, $(NH_2)_2CO \cdot HNO_3$ and $(NH_2)_2CO \cdot H_3PO_4$. The chloride and sulphate salts melt without decomposition [23], and $(NH_2)_2CO \cdot H_3PO_4$ is stable up to



Scheme 4.

120–185°C [24]. This relative stability is also due to the resonance structures **Va, Vb** and **Vc** (see scheme 4).

The positive charge on the nitrogen atom (structure **VI**) cannot be distributed over the rest of the molecule via a resonance mechanism. This structure is much less stable than structures **Va, Vb** and **Vc**, and although it was proposed originally [37], X-ray analysis proved the contrary [25]. In fact, a crystal structure analysis of uronium nitrate ($(NH_2)_2CO \cdot HNO_3$) shows that the acidic proton lies on the carbonyl oxygen atom with an O–H distance of 1.006(3) Å and forms hydrogen bonds to a nitrate oxygen atom with an O–H $\cdots$ O distance of 2.596(2) Å. Four other hydrogen bonds of the type N–H $\cdots$ O join the uronium $[(NH_2)_2COH]^+$ and NO_3^- ions in a two dimensional network [25].

C. VIBRATIONAL SPECTRA OF UREA AND URONIUM

The Raman spectra of urea has been thoroughly studied by Ananthakrishnan [26] and Reitz and Wagner [27] in the solid state and by Kohrausch and Pongratz [28] and Otvos and Edsall [29,30] in aqueous solutions. The infrared spectra have also been investigated [16,17,31,32]. The normal coordinate treatment of the molecular vibrations has been published by Kellner [33] and by Yamaguchi et al. [32,34]. Kellner, however, did not use the correct structure for the urea molecule, but assumed that the urea molecule had its four hydrogen atoms out-of-plane. Yamaguchi calculated the in-plane vibrations only.

The urea molecule has eight atoms which leads to 24 degrees of freedom. Taking into account the six non-genuine motions (three translations + three rotations) 18 internal modes of vibration are to be considered. Urea has C_{2v} point group symmetry if the four hydrogen atoms are in the plane of the molecule. The symmetry analysis is given below [1]

Total:	$8a_1 + 3a_2 + 5b_1 + 8b_2 = 24$
Rotational	$a_2 + b_1 + b_2 = 3$
Translational	$a_1 + b_1 + b_2 = 3$
Vibrational	$7a_1 + 2a_2 + 3b_1 + 6b_2 = 18$

The a_1 type vibration represents the symmetric vibration with respect to the C_2 axes and to the plane. Table 1 shows the overall results of vibrational analysis of urea and uronium cation and their appropriate descriptions taken from the literature [36]. The stretching frequency of the carbonyl vibration of urea is at 1686 cm^{-1} which does not correspond to a "free carbonyl". Indeed, acetone (CH_3COCH_3) shows a CO stretching vibration

TABLE 1

Vibrational analysis of urea and uronium cation [a]

Symmetry type	Frequency number	Urea-H_4		Urea-D_4		Infrared frequency (cm^{-1})		Description
		Observed (cm^{-1})	Calculated (cm^{-1})	Observed (cm^{-1})	Calculated (cm^{-1})	Uronium-H_5	Uronium-D_5	
$7a_1$	ν_1	3380				3446	2582	$NH_2(ND_2)$ sym. stretching
	ν_2	3150				3359	2440	$NH_2(ND_2)$ asym. stretching
	ν_3	1686	1648	1610	1597	1310		CO stretching
	ν_4	1603	1615	1245	1265	1651	1256	$NH_2(ND_2)$ bending
	ν_5	1150	1143	1001	986	1133	1021	$NH_2(ND_2)$ rocking
	ν_6	1000	1012	887	874	1015	876	CN sym. stretching
	ν_7	556	555	475	476	556	520	Skeletal deformation
$6b_2$	ν_8	3489				3437	2582	$NH_2(ND_2)$ sym. stretching
	ν_9	3230				3351	2378	$NH_2(ND_2)$ asym. stretching
	ν_{10}	1629	1639	1490	1477	1700	1620	$NH_2(ND_2)$ bending
	ν_{11}	1464	1461	1154	1174	1553	1167	CN asym. stretching
	ν_{12}	1150	1152	887	893	1130	875	$NH_2(ND_2)$ rocking
	ν_{13}	570	558	512	523	585	588	Skeletal deformation
	ν_{14}	785				743	713	$NH_2(ND_2)$ out-of-plane bending
$3b_1$	ν_{15}	717				645	500	CO out-of-plane bending
	ν_{16}	400				523	450	$NH_2(ND_2)$n wagging
$2a_2$	ν_{17}	490 [b]				inactive	inactive	CN out-of-plane bending
	ν_{18}	175 [b]				inactive	inactive	Skeletal deformation
Total:	18							
OH	ν_{19}					3295	1975	OH(OD) stretching
	ν_{20}					1350	943	OH(OD) bending in-plane
	ν_{21}							

[a] Taken from spectra published in ref. 36. [b] From ref. 179.

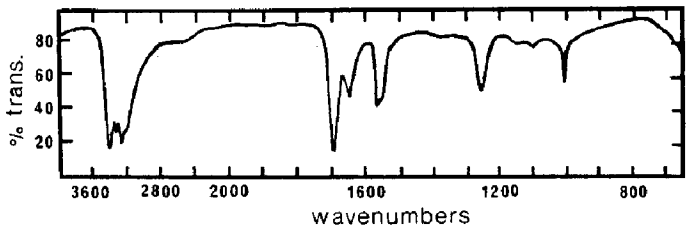


Fig. 2. The infrared spectrum of the solid ionic compound of urea, $[(NH_2)_2COH]_2[PtCl_6]$ in the 4000–670 cm^{-1} region.

frequency at 1715 cm^{-1} [35]. The resonance structures of urea (**Ia** and **Ic**) give rise to an average structure **II** for which the CO bond is less than the double bond. Moreover, the presence of hydrogen bonds between the carbonyl oxygen atoms and the hydrogen atoms, C=O · · · NH, in the solid [21] and in sufficiently concentrated solutions, induce indirectly the resonance equilibrium of urea (scheme 1), towards structures **Ia** and **Ic**. The protons withdraw electron density. Both effects lead to an increase in the C–N force constant and to a decrease in the C–O force constant [10,33].

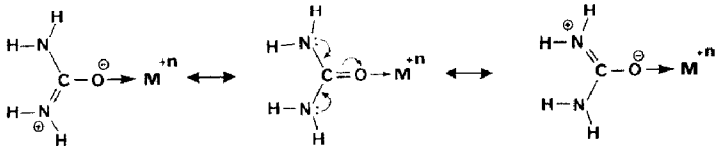
The acidic adducts of urea have also been investigated by infrared spectroscopy [37,36]. To our knowledge no work exists concerning the Raman spectra and normal coordinate calculations on the acidic adducts of urea. It appears that urea coordinates with the proton via an $O-H^+$ bond, forming the uronium cation. Kutzhing and Mecke [36] studied many salts with a wide variety of anions ($PtCl_6^{2-}$, $SnCl_6^{2-}$, $PtCl_6^{2-} \cdot 2\,H_2O$, $SbCl_6^- \cdot H_2O$, ClO_4^-, NO_3^-, $C_2O_4^{2-}$). The tetradeuterate urea used in the synthesis of urea–acidic adducts and deuterated uronium cations were also studied in this work. Figure 2 shows the infrared spectrum of solid $[(NH_2)_2COH]_2$-$[PtCl_6]$ in the 4000–670 cm^{-1} region, where the anion has no absorptions. Table 1 gives the vibrational analysis and description of cations $[(NH_2)_2COH]^+$ and $[(ND_2)_2COD]^+$. In addition, the vibrational frequencies have been averaged over the various salts and the differences between different salts are due to these intermolecular interactions between the uronium cation and the anions. The vibrational modes relating to the OH groups are discussed separately.

Table 1 shows that a new frequency appears at 3295 cm^{-1} which corresponds to the OH stretching vibration. The CO stretching vibration in urea is at 1686 cm^{-1}, while it is at 1310 cm^{-1} for the uronium cation. This indicates a shift of 20–30% toward single bond character of the carbonyl, i.e. to a highly single-bonded character, $C-O^-$ bond. Moreover, both C–N stretching frequencies shift to higher values especially that at 1464 cm^{-1} (ν_{11}) of urea which shifts to 1553 cm^{-1} for $[(NH_2)_2(OH)]^+$. This corresponds to a C–N bond with a high double bond character. The structures **Va**

and Vc are supported by these vibrational observations. A weak shoulder appears at about 1530 cm^{-1} in two of the spectra given in ref. 36, where the anions were $PtCl_6^{2-}$ and $PtCl_6^{2-} \cdot 2\ H_2O$. This could be assigned to an OH_2 bond. In general, each mode involving the NH or CN bonds increases in frequency while each mode involving the CO bond decreases in frequency when passing from urea to the uronium cation. The deuterated compounds do not show such large shifts in order to lead to similar conclusions.

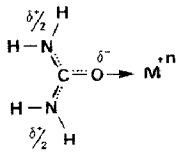
D. METAL–UREA COMPLEXES

One of the most interesting features of metal–urea complexes is the bidentate coordination of urea with metal atoms. Urea has three coordination sites: the carbonyl oxygen and the two nitrogen atoms. One direct way of determining the structure of these metal–urea complexes is by the crystallographic analysis of solid samples. However, when a crystallographic analysis is not available, vibrational spectroscopy (infrared and Raman) as well as NMR spectroscopy, gives information on bonding in the complexes. Urea, in spite of its three coordinating sites, usually acts as a monodentate ligand. The formation of unidentate oxygen–metal bonds between urea molecules and metal ions causes only minor changes in the infrared spectra of urea. Changes in the spectrum in this case are usually: (1) no great effect on the N–H stretching frequencies; (ii) a lowering of the C=O stretching frequency. However, the spectra differ significantly from that of free urea if a nitrogen–metal bond is present. The formation of an M–N bond increases



(VIIb) (VIIa) (VIIc)

n = 1,2,3,4, ...



(VIII)

Scheme 5.

electron demand of the nitrogen and also tends to block the resonance. These effects increase the C=O stretching frequency. The CN stretching frequencies are lowered as a result of blocking the resonance.

Many of these complexes have good thermal stability [38–45]. In order to explain the infrared and thermal properties of metal–urea complexes, where urea is bound to the metal through an O–M bond, consider scheme 5 showing the resonance structures of one urea ligand bound to a metal via an O–M bond. The oxidation state of the metal atom does not apparently change in these complexes (scheme 5).

In the following pages we have attempted to classify metal–urea complexes according to the periodic table; alkaline, alkaline-earth, transition, lanthanide and actinide metal–urea complexes. The reference numberings will be cited according to the progression of the atomic number of a metal–urea series, and may not be in increasing order in the following text.

(i) Alkaline metal–urea complexes

Stewart first discovered [46] large interactions between alkali halides and urea when mixed together as solid samples to form pellets for infrared analysis [46]. Chemical reactions occur between urea and CsBr, KI and KBr, while sodium halide remains unreactive in the presence of urea in the solid state. Many years later Alieva et al. studied Li, Na and Cs urea complexes in CD_3OD solutions by infrared spectroscopy [47]. The spectra of the solid samples were different from those recorded in solution. In solution, the compounds decomposed completely to the original components. Crystallographic analysis of some complexes afforded stronger evidence for metal–oxygen interactions. Verbist et al. studied the lithium iodide urea complex [48]. In the crystal, the urea molecule is bound to two lithium atoms at distances of 1.882 and 1.996 Å. The lithium–oxygen carbon angles are 149.4 and 120.2°. Another crystal was investigated by Polin et al. [49]. In this crystal the $NaCl \cdot urea \cdot H_2O$ complex has its urea oxygen bound to two sodium atoms, but with much weaker interactions. The Na–O bond distances were 2.465 and 2.496 Å. These bond distances are, however, too long for a normal coordination bond with a sodium atom. Similar weak metal–oxygen bonds have been observed only for U–O and La–O bonds in their metal–urea complexes (section D(iv)). The urea adduct in the Na crystal may be considered as a hydrated salt, $NaCl \cdot (H_2O)_n \cdot OC(NH_2)_2$, where $n = 6$, or coordinated, $[Na(H_2O)_6]Cl \cdot OC(NH_2)_2$.

(ii) Alkaline earth metal–urea complexes

Unlike alkali metal–urea complexes, the alkaline earth metal–urea complexes have been thoroughly investigated. The infrared spectra of mag-

nesium [41,50–53], calcium [50,51,54], and barium [47,51,55] urea complexes have been recorded and analysed by different groups. In all cases the urea oxygen atom is bound to the metal atom and the urea nitrogen atoms are not involved. For the complexes $Ca(NO_3)_2 \cdot CO(NH_2)_2$, $Ca(NO_3)_2 \cdot (CO(NH_2)_2)_4$, $CaCl_2 \cdot (CO(NH_2)_2)_4$, $BaCl_2 \cdot (CO(NH_2)_2)_4$ and $MgCl_2 \cdot (CO(NH_2)_2)_4$ the C=O stretching frequencies shift from 1686 cm^{-1} (urea ligand) to 1642–1665 cm^{-1}, while the NH_2 stretching frequencies remained unaffected [51]. To our knowledge, the beryllium and strontium–urea complexes have not yet been investigated by infrared spectroscopy and crystallographic analysis.

The crystallographic analysis of many alkaline earth metal–urea complexes has been published. Bond distances of 2.050 to 2.080 Å have been determined by Lebioda et al. for $[Mg(urea)_6]Br_2$ and $[Mg(urea)_4(H_2O)_2]Br_2$ [57–59]. The Mg–O–C angles were in the range 133 to 136° for the first complex and approximately 139° for the second. Calcium–urea complexes have also been thoroughly investigated [54,59–69]. The calcium nitrate tetraurea, $Ca(urea)_4 \cdot (NO_3)_2$ has its calcium ions octahedrally coordinated with two oxygen atoms from two nitrate ligands and four oxygen atoms from four urea ligands [66]. The metal–oxygen bond distances are about 2.300 Å and the metal–oxygen–carbon angles are in the range 144 to 151° [66]. The bond distances here are longer than those determined for Mg–O in Mg–urea complexes. The bond distances in other calcium–urea complexes are also in the same range: 2.351 Å ($Ca(NO_3)_2 \cdot 3\ H_2O \cdot$ urea) [68]; 2.315–2.330 Å $[Ca(urea)_6]Br_2$ [69]; 2.350–2.380 Å ($CaSO_4 \cdot 4$ urea) [70]. The M–O=C angles were in the range of 137.0° to 142.2° for the first complex and 131.6° to 139.1° for the second complex. It has been shown that the average angle is 137.6° [70] for alkaline earth metal–urea complexes. Lebioda [70] concluded that the urea molecule shows a strong preference to bind to divalent cations, along the directions of the lone-pair of electrons of the sp^3 hybridized O atom rather than along the direction of the dipole moment. Figure 3 shows the urea ligand bound to a metal atom and the different angles which can be considered. The angles ϕ and θ are respectively the angles between the M–O bond and the plane of the urea molecule and the angle between the C=O bond and the projection of M–O bonds on the plane

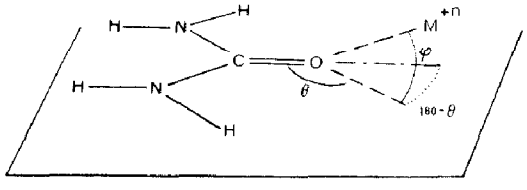


Fig. 3. A typical metal–urea complex with the angles θ and ϕ.

of the urea molecule. The angle ϕ is on average 6° excluding two exceptions (48.5° for one urea in $[Ca(urea)_6]Br_2$ and 38.3 for another). In general the M–O bonds are close to the urea molecular plane. The angle θ is very similar to the metal–oxygen–carbon angles as discussed earlier.

(iii) Post-transition and transition–metal urea complexes

The first row transition metal–urea complexes are certainly those which have been the most studied. Indeed the crystal structures of many urea–metal complexes such as those with Sc [71], Ti [72–77], V [78–80], Cr [81–89], Mn [90–93], Fe [81,94,95], Co [96–108], Ni [91,109–112], Cu [110,113–122] and Zn [122,63] have been studied. In all cases the urea ligand is bound to the metal atom through an oxygen–metal bond, except for a complex of urea–cobalt, $[Co(urea)_4](NO_3)_2$ [102], where urea acts as a bidentate ligand. Figure 4 shows the molecular structure of $[Co(urea)_4](NO_3)_2$. To our knowledge it is the only example in the literature, where a urea molecule binds to two metal atoms via two coordination sites; one from the oxygen atom and the other from the nitrogen atom (bidentate ligand). Figure 5 shows structures of $[Zn(urea)_6]^{2+}$ [123] and $[Ti(urea)_6]^{3+}$ [73]. It is clear that the M–O=C angles are not 180°. From a review by Lebioda [70] the average angle is 135.6°; Sc, 134.4°; Mn, 131.6°; Co, 131.0°; Cu and Zn, 131.6°. The metal atom "size" or metal atom oxidation state does not seem to have a large influence on this angle. The only difference is the M–O interatomic bond distance which increases with the metal atom "size". From ref. 70 the M–O distances are in the range: Sc–O, 2.077 to 2.134 Å; Mn–O, 2.001 to 2.076 Å; Zn–O, 2.073–2.1 Å (La–O, 2.46 Å).

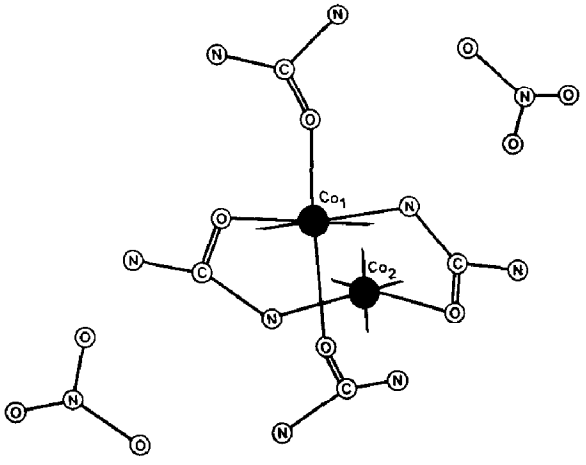


Fig. 4. Structure of $[Co(NH_2CONH_2)_4](NO_3)_2$ from ref. 65.

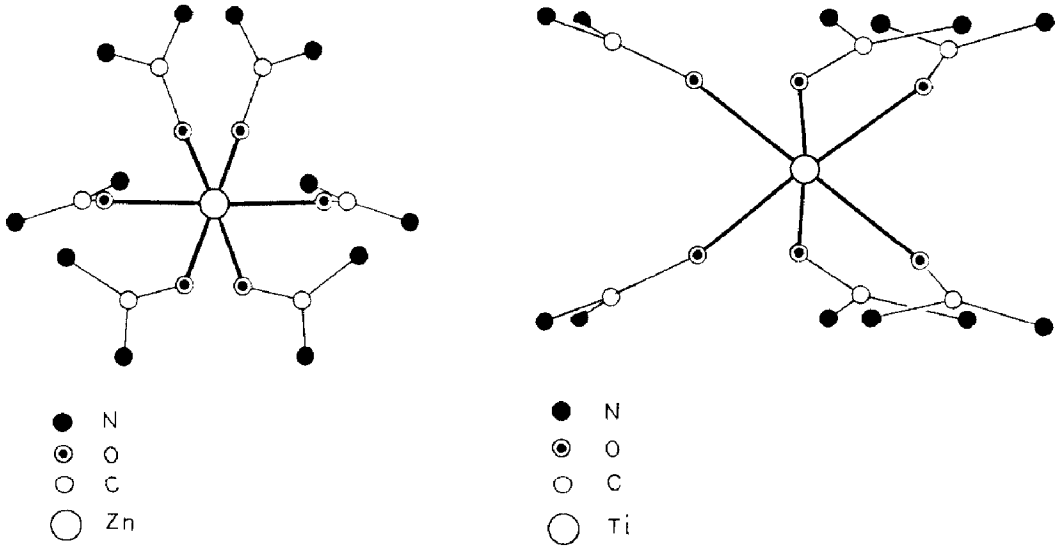


Fig. 5. Structure of $[Zn(NH_2)_2CO)_6]^{3+}$ from ref. 73 and $[Ti((NH_2)_2CO)_6]^{3+}$ from ref. 56.

Unfortunately, for the second and third row transition-metals the crystal structures seem to have been poorly investigated. Only the post-transition metal–urea complexes Cd [63,124–127] and Sb [128] have been published. On the other hand, the IR spectra of transition metal–urea complexes have been studied extensively (first, second and third row). Infrared studies on metal–urea complexes include Ti [129–133], V [134–137], Cr [47,52,137–139], Mn [47,51,52,91,140–145], Fe [47,52,137,146,147], Co [47,142,145,148,149], Ni [47,145,150–152], Cu [52,141,145,151–155], Zn [47,52,137,145,152,153, 156–159], Al [159], Ga [168], Ge [169,170], Y [171–173], Zr [159,130], Mo [160], Ru [161], Rh [161–163], Pd [47,137], Ag [47,52,164], Cd [52,125,133, 142,143,157,165,166], Sn [133,159,165–167], Sb [128], La [171,174,175], Hf [130], Re [176] by EPR, Pt [137,161], Hg [51,177] and Tl [178]. Figure 6 shows a comparison of the Fourier Transform infrared spectra of a Pt–urea complex and free urea at room temperature [179] and Table 2 surveys the vibrational data. An increase of the $\nu C{=}O$ stretching vibration and a decrease of the NH_2 stretching vibrations are the first indications of a nitrogen–metal bond in this complex [179].

Table 3 summarizes the CO and NH_2 vibrations of the various species found in several metal–urea complexes. Table 4 shows the coordination sites of urea when complexed to a metal in the Periodic Table. The coordinating sites of urea complexes with all the Periodic Table metals have been summarized in this Table and the references for each metal in Table 5. The identification and characterization of the metal–urea bonds have been made by X-ray or IR analysis and one given in Table 5. In Tables 6, 7 and 8

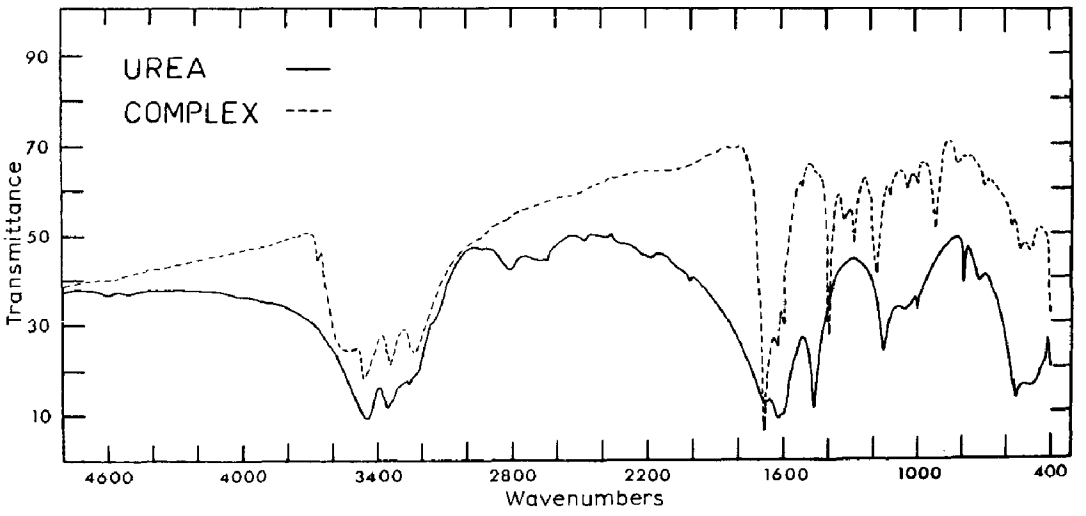


Fig. 6. Comparison of FT–IR spectra of urea and its platinum complex in the solid state in the 4800–400 cm^{-1} region from ref. 179.

references are given for the various metal groups of the Periodic Table. From Table 4, it is clear that all hard Lewis acids, alkali and alkaline-earths are linked to urea via the oxygen atom, while the soft Lewis acids are linked to the monodentate ligand via a metal–nitrogen bond (Co and Pt) and occasionally via a metal–oxygen bond. For Ni and Cu we found only the oxygen atom as a coordinating site, while for Pd and Ag only the nitrogen atom served as a coordinating site. Usually, Co links urea molecules via a Co–O bond except in one case (see Fig. 4). For Hg and Pt, both kinds of complexes, M–N and M–O have been observed [177] and this was supported by NQR investigations. Surprisingly, W, Au and Pb–urea complexes do not seem to have been investigated. However, for these and the other uncommon transition metals (Ta, Os, Ir) and frontier or post-transition metals (In, Pb, Bi, Po, Te, As, At) urea complexes should exhibit a metal–oxygen bond, where urea is monodentate. For the soft Lewis acid Au, we expect to see both M–N and M–O coordination in its complexes.

To our knowledge, no crystallographic work on metal–urea complexes, where the metal binds to the monodentate urea via the nitrogen atom has been reported. For such bond distances and angles, the reader should refer to the work on $[Co(NH_2CONH_2)_4](NO_3)_2$ [102]. The Co–N–C distance is 2.231 Å and the Co–N–C angle is 113.54° [73]. The Co–N bond is longer than the Co–O bond (see text above), which might be characteristic of some weakness of the M–N bond in urea–metal complexes. Since urea is bridging two different metals, the strain may induce lengthening in bond distances. In this case the Co–O (monodentate) bond distance is smaller than the Co–O

TABLE 2

Raman and FTIR spectra of a platinum–urea complex, $[PtCl_2(NH_2COHNH)_2]$

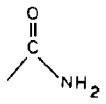
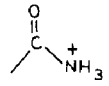
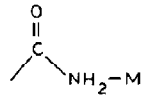
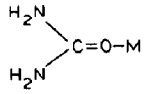
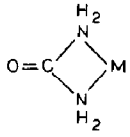
Pt–Urea Raman [a] (cm^{-1})	Pt–Urea IR (cm^{-1})	Assignment
	3560 s	O–H str. (water of cryst.)
	3450 vs	N–H asym. str.
	3340 s	N–H sym. str.
	3220 s	N–H · · · H-bonded
1655 w	1680 vs	C=O str. + δNH_2 asym.
1590 w	1610 s	C=O str. + δNH_2 sym.
–	1585 ms	δNH_2 coordinated
1480 w	1385 s	C=N str. asym.
1210 sh		
	1280 m	
1180 w	1180 s	NH_2 in-plane rocking asym.
1150 sh	1130 s, sh	NH_2 in-plane rocking sym.
1060 w	1044 w	
	1000 w	C=N sym. str.
	918 m	
800 m	810 m	
	690 m	
600 m	565 ms	δ(NCO)
	525 ms	Pt–N asym. str.
490 ms	500 ms	
440 vs	404 m	Pt–N sym. str.
330 vs	325 vs	Pt–Cl sym. str.
	195 s	δ(NPtN)
	170 s	δ(ClPtCl)
	115 s	
	95 s	

[a] s, strong; vs, very strong; m, medium; ms, medium-strong; sh, shoulder; str., stretch; sym., symmetric; asym., asymmetric. For a synthesis and structure determination of this Pt–urea complex see ref. 179.

(bidentate binding) bond distance (2.055 and 2.100(9) Å [102]), which is still smaller than 2.231 Å for the Co–N bond. The Co–N–C angle is also very different from that of Co–O–C (134.28(60)°) for bidentate and 128.73(73)° for monodentate ligand angles. This very significant difference is simply due to the different hybridization character of the N atom in the urea molecule. Frequently, it is difficult to distinguish between an oxygen and a nitrogen atom by X-ray diffraction, the electronic densities being similar. The angles M–O–C and M–N–C can be used to confirm the presence of an O or N atom coordinating site. Like the O atom in urea, the metal links the N atom along the direction of electron lone pair. In general, the distortion of the monodentate urea molecule is insignificant. The average C=O and C–N

TABLE 3

Frequencies of the functional groups of metal–urea complexes (cm^{-1})

Species	ν N–H [a]	ν C=O [b]
	3490 to 3150	1685 ± 15
	3050 to 2850	1700 ± 15
	3150 to 3050	1725 ± 15
	3500 to 3150	1645 ± 15
	3150 to 3050 [c]	1780 ± 15 [c]

[a] Average values taken from literature. [b] Indicates the range. [c] Empirically predicted values from model molecules.

bond distances are 1.250, 1.251 Å (Mg^{2+}), 1.258, 1.264 Å (Ca^{2+}), 1.339, 1.335 Å (Zn^{2+}), and 1.336, 1.333 Å for Sc^{3+} complexes [70]. The free urea molecule exhibits C–O and C–N bond distances of 1.26 ± 0.01 and 1.34 ± 0.02 Å [3,7] respectively. On the other hand, Lebioda [70], observed a systematic deformation in these structures, where the O–C–N angles are slightly greater on the cation side than on the opposite site to the cation. The average values are 121.8° and 120.6° for the transition–metal complexes. This is explained simply by a slight steric effect repelling the amino group.

(iv) Lanthanide and actinide metal–urea complexes

For the lanthanide series of metal–urea complexes see Periodic Table 4. There are only a few publications where the crystal and molecular structure has been analyzed; for example, the Ce–urea complex [183–185]. The other rare-earth metal complexes have been studied by IR spectroscopy [171,175,187,189,191]. These metals are hard Lewis acids and have the oxygen atom of urea as a coordination site. The Ce–O bond distances in the $Ce(SO_2)(urea)_2 \cdot 5\ H_2O$ complex [185], are 2.317 and 2.322 Å and the C–O–C angles are 176.2° and 153.6°. The analogous La–O bond distance and La–O–C angle in the $[La((CH_3)_2CO)urea] \cdot urea$ complex [186], are

TABLE 4

The coordination sites of urea in metal–urea complexes

O–H																
O–Li	Be										B					
O–Na	O–Mg										O–Al	N–Si				
O–K	O–Ca	O–Sc	O–Ti	O–V	O–Cr	O–Mn	O–Fe	O–Co	O–Ni	O–Cu	O–Zn	Ga	Ge	As		
Rb	Sr	Y	O–Zr	Nb	O–Mo	Tc	O–Ru	O–Rh	N–Pd	N–Ag	O–Cd	In	O–Sn	O–Sb	Te	
O–Cs	O–Ba	O–La	Hf	Ta	W	O–Re	Os	Ir	N–Pt	Au	O–N–Hg	Tl	Pb	Bi	Po	At
Fr	Ra	Ac		Ha												

O–Ce	Pr	O–Nd	Pm	Sm	O–Eu	O–Gd	O–Tb	O–Dy	O–Ho	O–Er	O–Tm	O–Yb	O–Lu
O–Th	Pa	O–U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

TABLE 5

Techniques used in the study of metal–urea complexes together with appropriate references

Metal X-ray	IR (+ others)
H	36, 78
Li 41	40, 79
Na 42	40, 39, 79
Mg 46, 47	40, 43–45, 78, 79, 80
Al 94	96
Si	95
K	39
Ca 48–53	40, 44, 79, 80
Sc 55	
Ti 56, 57, 88	74, 75, 93
V 58	76
Cr 59, 60	77–79
Mn 61	76, 78–81, 89, 91
Fe 57	77–79
Co 62–66, 86	79–82, 92
Ni 68, 69	79, 81, 83, 84, 90
Cu 70–72	77, 79, 81, 84, 85, 87, 89, 90
Zn 73	77, 78, 79, 81, 84–86
Zr 73	96
Mo	108
Ru	97
Rh	97
Pd	77, 78
Ag	78
Cd 98–100	78, 101–104
Sn	93, 96, 101–104
Sb 106	96, 105, 106
Cs	39, 40, 79
Ba	40, 44, 79, 80
La 107	79
Re	109 (EPR)
Pt	77, 97
Hg	80, 110 (NQR)
Ce 111	79
Nd	90
Eu	90
Gd	90
Tb	90, 112
Dy	112
Ho	112
Er	90, 112
Tm	112
Yb	90
Lu	112
Th	113
U 118–120 (electron diffraction)	114–117 (Raman), 121, 122

TABLE 6

Alkaline and alkaline–earth metal–urea complexes (and protonated urea)

Metal	References	
	Crystal and molecular structures	Infrared studies
H		36
Li	48	47
Na	49	47
Ca	56	46, 47
K		46
Mg	57–59	47, 50, 51, 52, 53
Ca	54, 59–68, 70	50, 51, 54
Ba	56	47, 55

2.461 Å and 162.9°. These two complexes show bonding at the metal cations along the dipole moment direction of the urea molecule and are, therefore, exceptions. Lebioda [70] claimed that such bonds are due to the metal oxidation state. Indeed these two latter complexes both have an oxidation state of **III**, while those discussed in the previous sections (4.2 and 4.3) have an oxidation state of **II** (in which the M–O–C angle is 130–135°). Unfortunately, this trend is not general, since in $[Sc(III)(urea)_2(NO_2)_2]NO$, the average M–O–C angle is 141°.

Only a few metal–actinide series metal–urea complexes are known. The Th–urea complexes have been synthesized and investigated by IR spectroscopy [192], where the thorium coordinates to urea via the oxygen. The only other metal in this series whose urea complex has been studied is uranium. Many research groups have been investigating the UO_2 complexes (in particular $[UO_2(urea)(H_2O)]NO_2$ and $[UO_2OH(urea)]$) which show that the M–O–C angles are again in the 133.8–144.8° range [206,209]. The complexes $[UO_2(urea)(H_2O)](NO_2)$ [120], $[UO_2F_2(urea)]$ [209] and $[UO_2OH(urea)]I$ [206] were investigated. In agreement with all previous infrared work, the uranium metal atom is linked to the oxygen atom of the urea molecule. Investigations with these radioactive metals is difficult because there is a relative radioactive instability apart from their high unavailability and cost.

E. FUTURE PERSPECTIVES

The aim of this review is to discuss the structural and dynamic behavior of metal–urea complexes. The nature of the bonding has been characterized mainly by X-ray crystallographical analysis and vibrational spectroscopy. The nature of the metal–urea bond has been well investigated, but more knowledge of the bidentate character of this ligand is required.

TABLE 7

Transition metal and post-transition metal-urea complexes

Metal	Reference nos.		
	X-ray (crystal and molecular)	IR studies	UV, luminescence, magnetic susceptibility electron spin resonance, NMR, Mossbauer
Se	71		
Ti	72–77	129–133	217–225
V	78–80	134–137	226, 219, 221, 223, 227–230
Cr	81–89	47, 52, 138, 139	219, 220, 229, 231–244
Mn	90–93	47, 51, 52, 91, 137, 140–145	91, 144, 219, 245
Fe	81, 94, 95	47, 52, 146, 147	94, 95, 146, 147
Co	96–108, 127	47, 142, 145, 148, 149	149, 107, 219, 246, 247
Ni	109–112	47, 145, 150–152	219
Cu	110, 113–122, 155	52, 141, 145, 151–155	114
Zn	123, 63	47, 52, 145, 152, 153, 156–159	
Al	180	159	220, 226, 238, 240, 248–250
Ga		168	240, 248–250
Ge		169, 170	
Y		171–173	
Zn	127	130	
Mo	181	160	
Ru		161	161
Rh		161–163	
Pd		47, 137	
Ag		47, 52, 164	164
Cd	63, 124–127, 112	52, 125, 133, 142, 143, 157, 165, 166	
Sn	167, 182	133, 159, 165–167	167, 182
Sb	128	128	128
La	174, 186	171, 174, 175	
Hf		130	
Re		176 (RPE)	
Pt		137, 161	161
Hg		51, 177	
Tl		178	
Si		251	

In the near future, we would be greatly interested in probing the behavior of certain metal-urea complexes in biological systems. Information on topics such as the concentration effects of complexes accumulated in biological systems, the possibility of further reaction, type of environment, nature of bonding between the complexes and the biological sites is needed. These effects can be evaluated by ultraviolet and visible spectroscopy,

TABLE 8

Lanthanide metal–urea complexes

Metal	Reference nos.		
	X-ray	IR studies	UV, luminescence
Ce	174, 183–185	171, 175, 189	189
Pr	188, 174	171, 187, 189	189
Nd	151, 174, 190	171, 175, 189	189
Pm		189	189
Sm	174	171, 175, 189	189
Eu	151, 174	171, 189	189
Gd	151, 172	171, 189	189
Tb	151, 172, 173, 191	171, 189, 191	189
Dy	172, 173, 191	171, 189, 191	189
Ho	172, 173, 191	171, 189, 191	189
Er	151, 172, 173, 191	171, 189, 191	189
Tm	172, 173, 191	171, 189, 191	189
Yb	151, 172, 173, 191	171, 189, 191	189
Lu	172, 173, 191	171, 189, 191	189
Th		192	
U	194–209	193, 210–212 215, 216	214
Pu	213		

magnetic susceptibility, electron spin resonance, multinuclei NMR spectroscopy, luminescence and photophysics. So far, these methods have been applied to a small number of urea complexes, but only for characterization purposes. We have included a number of references [217–250] which may be used at the start of such projects.

Recently, it has been found that some Pt–urea complexes have antitumor activity [252] and biological applications [253], although further observations have not been made. Because of their square-planar structure, the platinum–urea complexes should have good antitumor activity (e.g. *cis*-platinum). The NH_2 and CO groups should provide enough hydrogen bonding to produce conformational changes in nucleotides and DNA in addition to chemical bonding.

F. CONCLUSION

In this review we have tried to give a simple approach to understanding the physico-chemical and dynamic properties of urea and metal–urea complexes. The work summarized here may be useful for further structural and spectroscopic studies in this area. The paper summarizes important aspects of the field of urea–metal complexes, which should be investigated further in

order to understand better the bond and angle distortions, and the C–O and C–N vibrational frequency shifts, hybridization, dipole moment and oxidation states of the metals involved.

In the references selected, several physical techniques with which the metal–urea complexes can be studied are described. We have attempted to summarize work on crystallography and vibrational spectroscopy. These techniques are powerful tools in answering relevant questions, such as affinity, hydrogen-bonding, crystal and molecular structures. This information may lead to more research in this area and to the discovery of new metal–urea complexes with potential applications in medicine.

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