

Spectroscopic Studies of the Complexes of Urea with Group(II) Metal Halides

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Summary: The infra-red spectra, between 4000-400 cm^{-1} , and the Raman spectra, between 1700-950 cm^{-1} , of all the complexes of urea with group II metal halides are recorded to distinguish the mode of coordination of urea in these complexes. The e.s.r. spectra, at both X- and Q-band, of Mn(II) ions doped in these complexes are reported and the zero-field splitting parameters D and λ ($=E/D$) are deduced. For anhydrous complexes, with 1:4 stoichiometry, the observed D and λ values are consistent with trans- MO_4X_2 chromophores. Very small values of D observed for the hydrated analogues suggest an MO_6^{2+} chromophore. For 1:6 complex of CaCl_2 , the value of D and λ is exactly similar to that of $\text{Ca}(\text{urea})_4\text{Cl}_2$, suggesting similar structure. For all other complexes of 1:6 stoichiometry, the observed values are consistent with a coordination sphere of six oxygen atoms.

Introduction

Urea, a product of the metabolism of proteins, is excreted in human urine in average amounts of 30 g/day. It is used intravenously as an osmotic diuretic for the reduction of intracranial pressure and of intraocular pressure. It is also used topically to hydrate and remove excess keratin from dry skin [1].

Although, a number of complexes of urea with group (II) metal halides have been synthesized [2] and the crystal structures of three of them have been reported [3-5], spectroscopic studies of these complexes have received very little attention. Only the infra-red spectra of a few of them have previously been reported [6].

Here, we report the infra-red, Raman and e.s.r. studies of the complexes of urea with group (II) metal halides. The mode of coordination of urea in these complexes has been established by infra-red and Raman spectra and their structures have been studied by the e.s.r. spectra of Mn(II) doped complexes.

Results and Discussion

Vibrational spectra

The characteristic bands in the infra-red (4000-400 cm^{-1}) and the Raman spectra (1700-950 cm^{-1}) of urea and all of its complexes with group (II) metal halides are listed in Table 1. The infra-red and Raman spectra of the free ligand, in the solid state, have previously been carried out to assign the bands [8-9] and

Table 1: Characteristic vibrational spectra bands of urea complexes

Compound	CO/Stretch (Amide I)	H_2N Bend (Amide II)	CN Stretch	
			Asym.	Sym.
Urea (Solid)	IR 1682 S	1600 S	1462 S	1000 W
	R 1649 S	1578 W	1468 W	1010 VS
$\text{Mg}[(\text{urea})_4(\text{H}_2\text{O})_2]\text{Cl}_2$	IR 1658 SBr	1582 M	1468 SBr	1017 W
	R 1655 W		1489 W	1019 VS
$\text{Mg}[(\text{urea})_4(\text{H}_2\text{O})_2]\text{Cl}_2$	IR 1660 Br	1575 M	1465 VS	1018 W
	$\text{Ca}(\text{urea})_4\text{Cl}_2$	IR 1664 S	1588 S	1468 VS
R 1662 M		1594 M	1490 M	1022 S
$\text{Ca}(\text{urea})_4\text{Br}_2$	IR 1661 S	1585 S	1469 VS	1018 W
	R 1663 W		1490 W	1022 VS
$\text{Sr}(\text{urea})_4\text{Cl}_2$	IR 1658 Br	1575 S	1466 VS	1010 W
$\text{Mg}[(\text{urea})_6]\text{Cl}_2$	IR 1659 SBr	1578 S	1465 VS	1008 W
$\text{Mg}[(\text{urea})_6]\text{Br}_2$	IR 1661 SBr	1580 S	1463 VS	1010 W
$\text{Ca}[(\text{urea})_6]\text{Br}_2$	IR 1658 SBr	1579 S	1464 VS	1015 W
$\text{Sr}[(\text{urea})_6]\text{Br}_2$	IR 1660 SBr	1578 M	1453 VS	1005 W
$\text{Cd}(\text{urea})\text{Cl}_2$	IR 1677 VS	1592 VS	1479 VS	1017 W
	R 1651 M	1572 M	1497 S	1020 VS
$\text{Cd}(\text{urea})\text{Br}_2$	IR 1673 VS	1585 S	1475 VS	1013 W
	R 1645 M	1567 M	1491 S	1017 VS
$\text{Hg}(\text{urea})\text{Cl}_2$	IR 1675 M	1576 S	1486 M	1011 W
		1540 M	1455 VS	
	R 1643 M	1555 M	1482 M	1014 VS
		1001 S		

are in very close agreement with the frequencies reported here.

Urea has three coordination sites, the carbonyl oxygen and the two nitrogen atoms of the amide groups. The formation of an oxygen-metal bond increases the C=O bond length and decreases the C-N

bond lengths. As a result, the carbonyl frequency of the urea should decrease and the C-N stretching frequencies should increase. On the other hand, if a nitrogen-metal bond is formed, the spectrum of the complex would differ significantly from that of the free ligand. The N-H stretching frequencies will decrease and the carbonyl stretching frequency will shift towards the higher frequency.

In the infra-red spectra of all of these urea complexes, the frequency of carbonyl stretching vibration (at 1682 cm^{-1} in the ligand) decreases considerably, indicating that the urea molecules have been coordinated with the metal ions through their carbonyl oxygens. The frequency of the urea band at 1600 cm^{-1} , in the infra-red spectrum, and at 1578 cm^{-1} , in the Raman spectrum, which has been assigned as the mixed vibration of NH_2 bending and $\text{C}=\text{O}$ stretching modes [8-9], also decreases quite considerably on coordination.

Further, in the infra-red and Raman spectra of all of these complexes, the C-N stretching bands appear at higher frequencies compared with the free ligand. All these band shifts, on complex formation, are consistent with a decreased $\text{C}=\text{O}$ bond order and an increased C-N bond order.

In the infra-red spectra, the NH_2 stretching vibrations of urea in the region $3500\text{-}3150\text{ cm}^{-1}$, appeared at lower frequencies in the magnesium, calcium and strontium complexes and at higher frequencies in the cadmium and mercury complexes, suggesting that in the Mg, Ca and Sr complexes the hydrogen bonding has been decreased compared with the free ligand, whereas, in the Cd and Hg complexes the hydrogen bonding has been increased.

Electron spin resonance spectra

E.s.r. spectra have been obtained at both X- and Q-band frequencies for 1% manganese (II) ions doped into the lattices of compounds $\text{Ca}(\text{urea})_4\text{X}_2$ ($\text{X} = \text{Cl}$ and Br), $\text{Sr}(\text{urea})_4\text{Cl}_2$, $\text{Mg}[(\text{urea})_4(\text{H}_2\text{O})_2]\text{X}_2$ ($\text{X} = \text{Cl}$ and Br), $\text{Ca}[(\text{urea})_4(\text{H}_2\text{O})_2]\text{Br}_2$, $\text{Ca}[(\text{urea})_4\text{Cl}_2] \cdot 2\text{urea}$, $\text{Mg}(\text{urea})_6\text{X}_2$ ($\text{X} = \text{Cl}$ and Br), $\text{M}(\text{urea})_6\text{Br}_2$ ($\text{M} = \text{Ca}$ and Sr) and $\text{Cd}(\text{urea})\text{Cl}_2$.

At X-band frequency, all the complexes gave very good quality but complicated spectra (Fig. 1), with considerable overlapping of transitions and detailed interpretation was difficult. The strong transitions, near zero field, observed for the complexes $\text{M}(\text{urea})_4\text{Cl}_2$ ($\text{M} = \text{Ca}$ and Sr) suggested D values of about $0.1\text{-}0.2\text{ cm}^{-1}$. The X-b and spectrum of

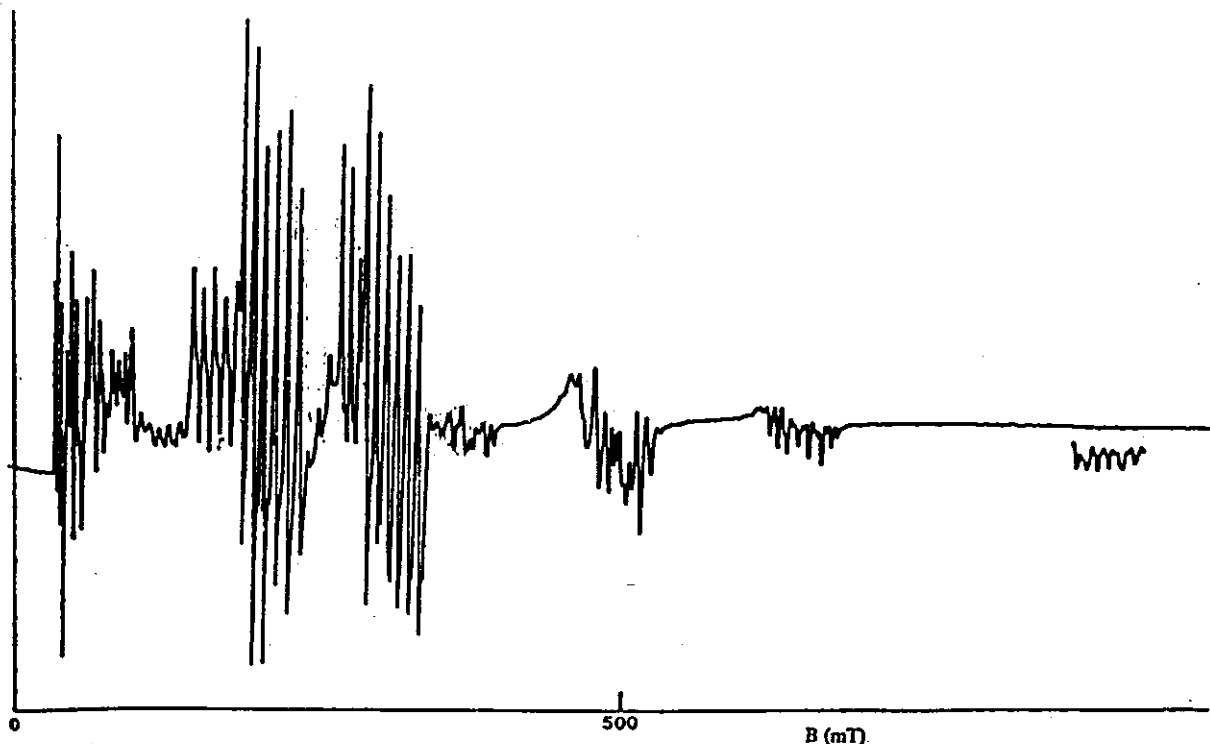


Fig.1: X-band ESR spectrum of $\text{Sr}(\text{Mn})(\text{urea})_4\text{Cl}_2$.

$\text{Ca}(\text{urea})_4\text{Br}_2$ was much simpler in form, with the main intensity near $g_{\text{eff}} = 2$ region, indicating a much g_{eff} higher value of D and a low but finite λ .

In contrast, the X-band spectra of all the hydrated complexes, with 1:4 stoichiometry, are very similar to one another, and of the same general type. The strongest bands occurred in the $g_{\text{eff}} = 2$ region, indicating much lower D values and the highest band observed around 475 mT, in the X-band spectra of Mg complexes, suggested D values of about 0.031 – 0.035 cm^{-1} .

The Q-band spectra of all complexes, with 1:4 stoichiometry, were much better resolved (Fig. 2) and therefore, were used to determine the precise value of D and λ ($= E/D$), for the individual compounds, in the Spin Hamiltonian (1).

$$= g\beta\text{BS} + D(\text{Sz}^2 - 3\text{S}^2/12) + E(\text{Sx}^2 - \text{Sy}^2) \quad (1)$$

The observed resonance fields fitted very well with those calculated, using the program ESRS [10], by exact diagonalization of the matrix derived from (1) with $g_{\text{iso}} = 2.00$ (Tables 2-3).

Table 2: Q-band ESR spectrum (mT) of $\text{Sr}(\text{Mn})(\text{urea})_4\text{Cl}_2$

Observed. ($\nu = 33.895 \text{ GHz}$)	Calculated for $D = 0.134 \text{ cm}^{-1}$, $\lambda = 0.003$			
	B.	T.P.	Field Direction	Levels
636.2 W	636.8	5.01	Z	2-1
Region	665.2	0.65	$\theta=61^\circ, \phi=00^\circ$	4-2
642-692 ^W	667.3	0.66	$\theta=61^\circ, \phi=90^\circ$	4-2
Region	767.7	0.45	$\theta=17^\circ, \phi=00^\circ$	5-3
743-794 ^W	768.3	0.45	$q=17^\circ, \phi=90^\circ$	5-3
924.7 M	923.8	8.01	Z	3-2
943.9 W	943.8	3.88	Y	6-5
950.2 W	949.1	3.88	X	6-5
1050.4 M	1051.6	6.87	Y	5-4
1053.2 M/S	1053.8	6.86	X	5-4
	1177.7	8.63	X	4-3
1177.9 S				
	1178.1	8.62	Y	4-3
1211.2 S	1210.8	9.00	Z	4-3
1327.3 S	1326.1	8.67	X	3-2
1330.6 S/M	1329.0	8.66	Y	3-2
1498.1 M	1497.8	8.00	Z	5-4
1507.3 M/W	1507.4	6.20	X	2-1
1512.8 W	1512.4	6.19	Y	2-1
1785.7 W	1784.8	4.99	Z	6-5

The positions of the off-axis transitions were calculated for the Q-band spectra of many of these

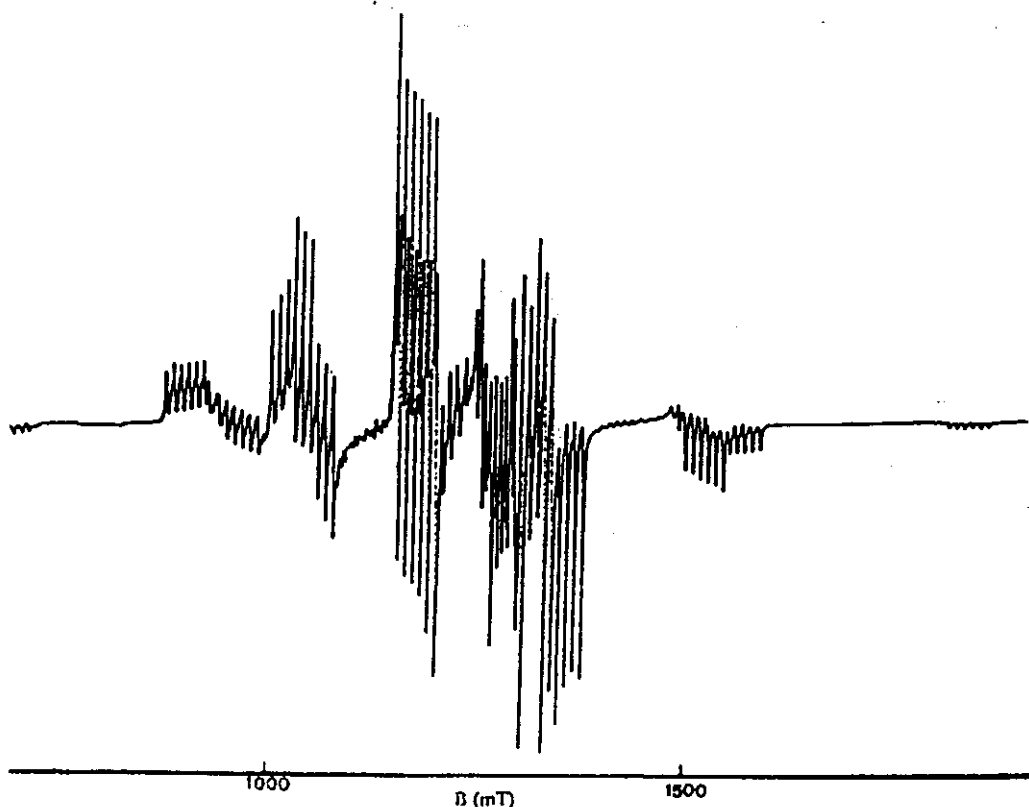


Fig. 2: Q-band ESR spectrum of $\text{Ca}(\text{Mn})(\text{urea})_4\text{Cl}_2$.

Table 3: Q-band ESR spectrum (mT) of Mg(Mn)(urea)₆Br₂.

Observed ($\nu = 33.900$ GHz)	Calculated for $D = 0.023$ cm ⁻¹ , $\lambda = 0.246$.			
	B.	T.P.	Field Direction	Levels
1114 W	1113.5	5.10	Z	2--1
1127 W	1126.4	4.85	Y	6--5
1163 M	1162.0	8.08	Z	3--2
1169 M	1168.2	7.87	Y	5--4
Region of overlap	1199.0	4.75	X	6--5
1209 S	1203.6	7.80	X	5--4
	1209.5	8.99	X	4--3
	1210.4	8.99	Y	4--3
1210 S				
	1210.7	9.01	Z	4--3
1215 S/M	1216.4	8.20	X	3--2
Region of overlap	1224.5	5.26	X	2--1
	1253.0	8.11	Y	3--2
1259 M	1259.7	7.93	Z	5--4
1296 W	1296.1	5.15	Y	2--1
1309 W	1308.8	4.90	Z	6--5

Table 4: ZFS parameters of Mn(II) in complexes.

Complex	D (cm ⁻¹)	λ
1. Ca(urea) ₄ Cl ₂	0.145	0.035
2. Sr(urea) ₄ Cl ₂	0.134	0.003
3. Ca(urea) ₄ Br ₂	0.425	0.016
4. Mg[(urea) ₄ (H ₂ O) ₂]Cl ₂	+ 0.032	0.180
5. Mg[(urea) ₄ (H ₂ O) ₂]Br ₂	+ 0.031	0.250
6. Ca[(urea) ₄ (H ₂ O) ₂]Br ₂	0.019	0.225
7. Ca[(urea) ₄ Cl ₂].2 urea	0.145	0.035
8. Mg(urea) ₆ Cl ₂	+ 0.043	0.200
9. Mg(urea) ₆ Br ₂	0.023	0.246
10. Ca(urea) ₆ Br ₂	+ 0.019	0.220
11. Sr(urea) ₆ Br ₂ *	≤ 0.019	---
12. Cd(urea)Cl ₂	- 0.046	0.080

*Too small to evaluate.

complexes and fitted very well with the weak bands observed at low field.

Values of D and λ are listed in Table 4. For the anhydrous complexes with 1:4 stoichiometry, the observed D and λ values are consistent with trans-MO₄X₂ chromophores (M = Ca, X = Cl and Br; M = Sr, X=Cl). The lower D value for Sr(urea)₄Cl₂, compared with that of Ca(urea)₄Cl₂, is in line with the usual observation that D decreases as the size of the host metal ion increases. Further, the higher value of D found for Ca(urea)₄Br₂, than for chloride analogue, suggests that in all these anhydrous complexes halides are involved in the coordination. The low

values of λ observed for them confirm that these complexes have quite regular in-plane structures.

In contrast, the D and λ values observed for all the hydrated complexes, with 1:4 stoichiometry, are very similar to one another but entirely different from those of anhydrous analogues. The small values of D for these complexes indicate an MO₆⁺² chromophore.

For all the complexes of 1:6 stoichiometry, except CaCl₂ complex, the quality of both the X- and Q-band spectra, were sufficient enough to obtain the parameters D and λ which are also listed in Table 4.

For 1:6 complex of CaCl₂, the calculated value of D and λ is exactly similar to that of Ca(urea)₄Cl₂, suggesting that both complexes have similar structures. It seems likely that in CaCl₂ complex, of 1:6 stoichiometry, each calcium ion has been coordinated with four urea and two chloride ions and this complex can correctly be formulated as Ca[(urea)₄Cl₂]. 2 urea.

For all other complexes of 1:6 stoichiometry, the D and λ values are very similar to one another. The lower values of D observed for these complexes are consistent with a coordination sphere of six oxygen atoms. The higher values of λ observed for these 1:6 complexes suggest considerable deviation from axial symmetry. This result is consistent with the X-ray crystal studies of these hexakis urea complexes [5-6], where observed bond angles are far away from 90° (86-95° for Mg complex).

For the complex Cd(urea)Cl₂, the e.s.r. spectra were measured at both X- and Q-band frequencies and proved to be of sufficient quality to allow interpretation of D and λ . However, the higher frequency at Q-band results in better resolution and was preferred for determination of D and λ .

The observed values of D = 0.046 cm⁻¹ and $\lambda = 0.08$ for Cd(urea)Cl₂ are consistent with the values previously reported for manganese(II) ions doped in the analogous chloride-bridged polymers CdLCl₂ (L = pyridine or substituted pyridine) [11], i.e. D = 0.06 cm⁻¹ and $\lambda = 0.04$. It is expected that D value would decrease when the nitrogen-coordinated ligand, pyridine, is replaced by oxygen-coordinated ligand, urea, since the oxygen donor is closer to chloride in the spectrochemical series, and thus produces less distortion along the principal axis.

Experimental

All of these complexes were prepared by the same general method. The hot aqueous solutions of hydrated metal salt and urea, in stoichiometric quantities, were mixed together and the resulting solution was filtered off. The mixture was allowed to evaporate slowly at room temperature for several days. The precipitates thus formed were filtered off, washed with ether and dried in vacuo at room temperature. Found:- C, 13.30; H, 5.48; N, 3.90. Calculated for $Mg[(urea)_4(H_2O)_2]Cl_2$:- C, 12.93; H, 5.39; N, 30.16. Found:- C, 10.44; H, 4.35, N, 24.26. Calculated for $Mg[(urea)_4(H_2O)_2]Br_2$:- C, 10.43; H, 4.35; N, 24.35. Found:- C, 13.93; H, 4.65; N, 31.85. Calculated for $Ca(urea)_4Cl_2$:- C, 13.68; H, 4.56; N, 31.91. Found C, 10.87; H, 3.64; N, 25.31, calculated for $Ca(urea)_4Br_2$; C, 10.91; H, 3.64, N, 25.40. Found:- C, 12.23; H, 4.03; N, 27.75. Calculated for $Sr(urea)_4Cl_2$:-C, 12.04; H, 4.01; N, 28.10. Found:-C, 15.41; H, 5.10;N, 35.71. Calculated for $Ca[(urea)_4Cl_2]_2$ urea:- C, 15.92; H, 5.10; N, 35.67. Found:- C, 15.73; H, 5.23; N, 36.52. Calculated for $Mg[(urea)_6]Cl_2$:- C, 15.81; H, 5.27; N, 36.90. Found:- C, 13.42; H, 4.48; N, 31.27. Calculated for $Mg[(urea)_6]Br_2$:-C, 13.23; H, 4.41; N, 30.86. Found: C, 13.13; H, 4.35; N, 29.97. Calculated for $Ca[(urea)_6]Br_2$:- C, 12.86; H, 4.29;N, 30.00. Found:- C, 11.89; H, 4.42; N, 27.70. Calculated for $Sr[(urea)_6]Br_2$:- C, 11.85; H, 3.95; N, 27.65. Found:- C,5.22; H, 1.65; N, 12.33. Calculated for $Cd(urea)Cl_2$:- C, 4.93; H, 1.64; N, 11.51. Found:- C, 3.71; H, 1.09; N, 8.44. Calculated for $Cd(urea)Br_2$:-C, 3.61; H,1.20; N, 8.42. Found:- C, 3.70; H, 1.13; N, 8.40. Calculated for $Hg(urea)Cl_2$:- C,3.62; H, 1.21; N, 8.45.

Analytical results were obtained by the Imperial College Microanalytical Laboratory

Infra-red spectra were obtained using a Perkin-Elmer 1720 FTIR spectrometer. Raman spectra were

measured on a Spex Ramalog-V spectrometer and Spex Datamate computer control unit, using the exciting line at 568.2 nm from a Coherent Innova 90 Krypton-ion laser, and 488.0 nm from a Coherent Innova 70 Argon-ion laser. Spectra were taken from solid samples as spinning KBr discs.

For the ESR study the normal doping level was 1% of manganese in all cases. ESR spectra were obtained as described previously [7], using polycrystalline samples at room temperature.

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