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Coordination of Manganese(II): High Spin Complexes with Urea

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The following coordination compounds of Manganese(II) with urea have been prepared: MnU_2X_2 *(with* $X = Cl, Br$*),* MnU_4X_2 *(*$X = Cl, Br$*),* MnU_6X_2 *(*$X = Br$*, I and* ClO_4*) and* $MnU_{10}X_2$ *(*$X = Br, I$*). I.R. spectra (4000–200* cm^{-1}*), electronic spectra, paramagnetic susceptibility and powder diffraction patterns were studied. All these compounds are high-spin octahedral with urea coordinated through oxygen.* MnU_2X_2 *has chain-like structure with bridging halogen atoms.* MnU_4X_2 *is trans-octahedral;* $MnU_{10}X_2$ *is to be considered as* $[MnU_6]X_2 \cdot 4U$*, the four extra urea molecules being hydrogen bonded to the* MnU_6^{2+} *cation.*

Introduction

In a previous work we have studied several complexes of manganese(II) with N,N′-diethylurea[1] and N,N′-dimethylurea[2] and found mixed octahedral–tetrahedral compounds with DEU and only octahedral compounds with DMU. It was interesting to look now at the urea complexes which were practically unknown except for the octahedral MnU_4Cl_2.[3,4]

Experimental

All reagents urea and manganese salts were recrystallized in water. Manganese(II) iodide was washed with anhydrous benzene to eliminate the small excess of iodine. All preparations were done in anhydrous ethanol under a stream of nitrogen and for the iodides in the dark; 2,2-dimethoxypropane (DMP) was added to eliminate all traces of water.[5]

The obtained solids were washed with diethylether and dried under vacuum (0.2 mm) at room temperature. The yields were good (from 50 to 85%).

Dichloro and Dibromobis(urea)manganese(II)

Urea (0.04 mol, 2.4 g) was added to an ethanolic solution of manganese halogenide (0.02 mol). After two hours of refluxing, the chloride precipitated whereas the bromide gave an oil which crystallized after addition of cold diethylether.

Dichloro and Dibromotetrakis(urea)manganese(II) and Dibromo, Diiodo, Diperchloratohexakis(urea) manganese(II)

Stoichiometric amounts of reagents were stirred at room temperature during two hours. Cold diethylether was added to start crystallization. At higher temperature compounds with less urea were obtained.

Dibromo and Diiododeca(urea)manganese(II)

Stirring of solutions at room temperature with ratios urea/manganese higher than ten yielded always, after addition of diethylether, the compounds.

Analytical

Manganese was checked with EDTA at pH 10 in presence of eriochrome black T. The halogenides were determinated by potentiometry with silver nitrate (Table I).

Results and Discussion

Infra-red Spectra

I.R. spectra on solids in the 4000–400 cm^{-1} region were obtained in KBr discs or either Nujol mulls (to check the absence of the possibility of exchange of the halogen ions) and in polyethylene discs in the far infra-red (400–200 cm^{-1}).

Table II shows great analogies even if the compounds are different. Attributions are made following Stewart[6] and Penland *et al.*[7] The latter one showed how the evolution of the spectra of urea and coordinated urea can give indications on the nature of the coordinated ligand atoms. Coordination through nitrogen will give a new band around 3000 cm^{-1} and a large modification of the urea spectra, whereas coordination through oxygen will only slightly modify the urea spectra (ν(C=O) will decrease, ν_{sym} (C–N), ν_{asym} (C–N), ν(N–H) and δ(N–H) will increase).

It is difficult to take into account ν(N–H) because of hydrogen bonds present in urea as well as in the compounds: the hydrogen bonding will decrease ν(N–H). In MnU_2X_2 hydrogen bonds are inexistant or small, there is an increase of ν(N–H). In urea the band at 1680 cm^{-1} is assigned to ν(C=O) and the

TABLE I. Analytical Results.

Compound	Color	Melting Point °C	%Carbon		%Hydrogen		%Nitrogen		%Manganese		%Halogen	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
MnU_2Cl_2	Pink	dec. 215°	9.77	10.02	3.28	3.43	22.78	22.82	22.3	22.3	28.8	28.7
MnU_4Cl_2	Pale-pink	162°	13.12	13.30	4.41	4.53	30.61	30.66	15.0	14.9	19.4	19.2
MnU_2Br_2	Pink	207°	7.17	7.57	2.41	2.65	16.73	16.86	16.4	16.2	47.7	46.8
MnU_4Br_2	Pale-pink	150°	10.56	10.90	3.54	3.62	24.63	24.59	12.1	12.1	35.1	35.1
MnU_6Br_2	White	130°	12.53	12.76	4.21	4.40	29.23	29.37	9.5	9.5	27.8	27.7
$MnU_{10}Br_2$	White	117°	14.73	14.95	4.95	5.17	34.36	34.33	6.7	6.7	19.6	19.4
MnU_6I_2	White	158°	10.77	11.04	3.62	3.80	25.12	25.09	8.2	8.2	37.9	37.6
$MnU_{10}I_2$	White	121°	13.21	13.39	4.43	4.58	30.81	30.95	6.0	6.0	27.9	27.8
$MnU_6(ClO_4)_2$	White	190°	11.73	12.01	3.94	4.11	27.37	27.26	8.9	8.9		

TABLE II. Significant Bands in the Infrared Spectra of Coordinated Mn(II) Urea Complexes (4000–400 cm^{-1}).

Compound	ν(N–H) Stretching	ν(C–O) and δ(N–H) Stretching Bending	ν_{asym} (C–N) Stretching	ν_{sym} (C–N) Stretching
Urea	3460s 3350s 3250sh	1680s 1630 and 1600s	1465s	1000w
MnU_2Cl_2	3480s 3410s 3365s	1660sh and 1620s 1580s	1475s	1015w
MnU_2Br_2	3480s 3420s 3370s	1665sh and 1625s 1575s	1475s	1015w
MnU_4Cl_2	3460s 3330s	1620sb	1480s	1010w
MnU_4Br_2	3430s 3330s	1625sb	1470s	1010w
MnU_6Br_2	3420–3300–3200sb	1610sb	1470s	1015w
MnU_6I_2	3400–3300–3200sb	1610sb	1470s	1015w
$MnU_6(ClO_4)_2$	3470s 3370sb	1630sb	1470s	1010w
$MnU_{10}Br_2$	3410–3340–3200sb	1625sb	1480 and 1455s	1010w
$MnU_{10}I_2$	3410–3340–3200sb	1625sb	1480 and 1450s	1010w

Abbreviations: s, strong; w, weak; sh, shoulder; b, broad.

bands at 1630 and 1600 cm^{-1} to δ(N–H). There is a decrease of the stretching frequency of the carbonyl group in all the complexes but the position of the bending frequency δ(N–H) cannot be precised because of the coupling with ν(C=O). All this bandshifts are in agreement with a coordination through oxygen.

The low-energy spectra of all compounds show a large band at 380 cm^{-1} which is assigned following Ferraro[8] to a metal–oxygen vibration and a band around 240 cm^{-1}. That last band is split for MnU_2X_2. For MnU_4Cl_2, there is another band at 225 cm^{-1} assigned to a manganese–chloride vibration in an octahedral complex.[8]

The manganese–bromide or the bridging chloride or bromide vibrations being at energies lower than 200 cm^{-1}, they could not be detected with our instrument.[9]

Electronic Spectra

In manganese(II) compounds the intensities of electronic transitions from the ground state ^6S to states of fourfold multiplicity are very weak and therefore difficult to detect especially in reflexion spectra. Spectra of MnU_6X_2 and $MnU_{10}X_2$ could not be obtained on the solid. Two evident reasons for this are: first, the high O_h symmetry of the chromophore MnO_6 and second, the low concentration of the manganese(II) on the surface of the solid.

All other complexes are octahedral (Table III) in comparison with the spectra of typical octahedral compounds like $[Mn(OH_2)_6]^{2+}$, $Mn(OH_2)_4X_2$ and MnX_2 with X = Cl and Br. Orgel[10] and Heidt *et al.*[11] energy diagrams are not sufficient to account for the position of the bands and we must also introduce the nephelauxetic ratio β.

The β values for MnU_2X_2 correspond practically to the average of the β values for MnU_4X_2 (surrounding of Mn : 4 oxygens and 2 halogens) and MnX_2 (surrounding : 6 halogens). This suggests a two oxygens and four halogens surrounding and henceforth bridging halogen atoms. In addition, we compared β values calculated from the experimental data and from Jör-

TABLE III. Electronic Reflexion Spectra (wavenumbers in cm^{-1}).[a]

Transition $^6A_1 \rightarrow$ Compound	$^4T_1$ (^4G)	$^4T_2$ (^4G)	^4E+$^4A_1$ (^4G) ν_3	$^4T_2$ (^4D)	^4E (^4D)	$\beta = \nu_3/26846$ (ref. 12)	$\beta = 1-hk$
$Mn(OH_2)_6^{2+} (ClO_4^-)_2$	18850	22750	24900			0.93	0.93
MnU_6Br_2	(19050)		24700			0.92	0.92
$Mn(OH_2)_4Cl_2$	19250	22450	24350	27400		0.91	0.91
$Mn(OH_2)_4Br_2$	19050	22900	24100	27250		0.90	0.90
MnU_4Cl_2	(19400)	(22450)	24150			0.90	0.90
MnU_4Br_2	(19400)	(22450)	24150			0.90	0.89
MnU_2Cl_2	19450		23800	26900		0.89	0.88
MnU_2Br_2	19550		23450	26650	28000	0.87	0.87
$MnCl_2$	18700	21900	23300	26500	27450	0.87	0.86
$MnBr_2$	18650	21700	23050	26100	27050	0.86	0.84

[a] The numbers in parentheses correspond to very weak intensities.

gensen's[12] relation $\beta = 1-hk$ where h is a caracteristic of the ligand and k of the cation. We have a good agreement between the two β values.

Fluorescence

At room temperature, the compounds like MnU_2X_2 and MnU_4X_2 present a strong red fluorescence which is caracteristic of octahedral coordination of lower symmetry than O_h.[13, 14]

Magnetic Susceptibility

The paramagnetic susceptibility, at 20° C, is higher than 14700×10^{-6} cgs for all compounds except for MnU_2X_2. If we admit a Weiss constant near 0° K for most manganese(II) compounds, all the experimental values are close to the spin only calculated value 5.92 B.M. for high spin d^5 complexes (Table IV).

For the MnU_2X_2 compounds the paramagnetic susceptibilities χ_M are lower. In this case we measured the susceptibility from 77° K to room temperature, we have a straight line for $\chi^{-1} = f(T)$ with high Weiss constants: $\Theta = -22°$ K for the bromide and $\Theta = -42°$ K for the chloride. In these cases we have strong metal–metal interactions probably of ferromagnetic type. This is in agreement with a chain structure containing bridging halogen atoms. The higher value of Θ for MnU_2Cl_2 is due to the smaller distance between the metal atoms in MnU_2Cl_2 than in MnU_2Br_2.

TABLE IV. Magnetic Properties at 293° K.

Compound	Diamagnetic Correction	$\chi_M^{Corr} \times 10^6$ ±250 cgs	μ_{eff} in B.M.± 0.05
MnU_2Cl_2	114	14000	6.12[a]
MnU_4Cl_2	180	14700	5.87
MnU_2Br_2	136	13750	5.89[a]
MnU_4Br_2	203	14700	5.87
MnU_6Br_2	270	14750	5.88
$MnU_{10}Br_2$	403	15000	5.93
MnU_6I_2	302	15200	5.97
$MnU_{10}I_2$	435	14800	5.89
$MnU_6(ClO_4)_2$	264	14650	5.86

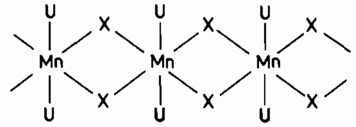
[a] Calculated value with $\Theta = -42°$K for Cl and $\Theta = -22°$K for Br.

Powder Diffraction Patterns

After comparison of the different powder diffraction patterns, we obtain four isostructural groups given on Table V. We compared also some structures of cobalt (II) complexes prepared in this laboratory.[15] Compounds $CoU_{10}X_2$ with X = Br and I studied by Sulejmanow *et al.*[16] are monoclinic (P 2_1/c).

Conclusion

From these physical studies we can conclude that all the prepared Mn(II) complexes with urea are high spin and octahedral. The MnU_2X_2 (X = Cl, Br) complexes have a chain-like structure with halogen bridges:



This is supported by the electronic spectra and the magnetic susceptibility data but could not be checked by I.R. spectroscopy, the Mn–X bridging vibration frequency lying below 200 cm^{-1}.

For the molecular complexes MnU_4X_2 (X = Cl, Br), the existence of a single vibration band Mn–Cl suggests an octahedral *trans*-structure.

The MnU_6X_2 (X = Br, I and ClO_4) compounds are ionic: $[MnU_6]X_2$.

For $MnU_{10}X_2$ with X = Br, I, we have also an octahedral structure around the manganese atom and not a tenfold coordination. The compounds should be

TABLE V. Isostructural Compounds.

MU_2X_2	MU_6X_2	$MU_{10}X_2$	$MU_6(ClO_4)_2$
MnU_2Cl_2	MnU_6Br_2	$MnU_{10}Br_2$	$MnU_6(ClO_4)_2$
MnU_2Br_2	MnU_6I_2	$MnU_{10}I_2$	$CoU_6(ClO_4)_2$ (Ref. 15)
CoU_2Cl_2 (Ref. 15)		$CoU_{10}Br_2$ (Ref. 15)	
		$CoU_{10}I_2$ (Ref. 15)	

written $[MnU_6]X_2\cdot4U$. The four extra molecules of urea are probably hydrogen bonded to the $[MnU_6]^{2+}$ cation and this is in agreement with the I.R. spectra.

We see that small anions like chloride favour the formation of small molecules like MnU_2Cl_2 and MnU_4Cl_2. Large anions like iodide and perchlorate stabilize the complex cation $[MnU_6]^{2+}$ whereas for bromide of intermediate size, we can obtain all types of complexes MnU_nBr_2 with $n = 2, 4, 6$ and even 10.

We note also that the stoichiometry MnL_3X_2 easily obtained with DMU and DEU[1,2] could never be prepared with urea.

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