Methyl Cyanide and NN-Dimethylacetamide Complexes of Thorium and Uranium Tetrahalides, Uranyl Chloride, and Uranyl Bromide

By K. W. Bagnail, D. Brown, and P. J. Jones

The tetrachloride and tetrabromide of thorium and of uranium react at room temperature with anhydrous methyl cyanide to form the complexes $MX_4.4CH_3CN$ (M = Th and U; X = Cl and Br). The tetrabromide complexes react with NN-dimethylacetamide (DMA) to form the compounds MBr₄.4DMA. Methyl cyanide and DMA complexes of uranyl chloride and uranyl bromide, $UO_2CI_2.CH_3CN$ and $UO_2X_2.2DMA$ (X = CI and Br) have also been prepared. Some chemical properties, infrared spectra, and magnetic susceptibilities are reported for these complexes.

WHEREAS thorium and uranium tetraperchlorate,^{1,2} tetranitrate,^{1,3} and tetrathiocyanate^{1,4} form isostructural pairs of complexes with NN-dimethylacetamide (DMA), the tetrachloride ^{1,5} complexes, UCl₄,2.5DMA and ThCl₄,4DMA, and the tetraiodide⁶ complexes, $ThI_4,6DMA$ and $UI_4,4DMA$, are quite different. In view of these differences and those recently observed ⁷ for the tetrachloride-dimethyl sulphoxide (DMSO) complexes, ThCl₄,5DMSO and UCl₄,3DMSO, and for the hexamethylphosphoramide (HMPA) complexes formed by the tetrabromides, namely ThBr₄,3HMPA and UBr₄,2HMPA, it appeared worthwhile to investigate the tetrabromide-DMA complexes. We have also studied the methyl cyanide complexes formed by thorium and uranium tetrachloride and by uranium tetrabromide because, although thorium tetrabromide⁸ and tetraiodide⁹ form the complexes

Tetrahalide Complexes.-The tetrachloride and tetrabromide of thorium and of uranium react exothermically with anhydrous methyl cyanide at room temperature to form the virtually insoluble, deliquescent complexes ThX_4 , 4CH₃CN and UX₄, 4CH₃CN (X = Cl and Br). Like the analogous thorium tetraiodide complex,⁹ these compounds start to lose methyl cyanide at $40-50^{\circ}$ in a vacuum and decompose directly to the tetrahalides, which are obtained above 200°; there is no evidence for thermally stable complexes between MX4,4CH3CN and MX_4 . As observed ¹¹ we find that the formation of the nitrogen-metal bonds results in an increase in the stretching frequency of the C=N triple bond. The value which we have recorded for the stretching frequency of the C=N bond in free methyl cyanide, 2249 cm.⁻¹, is in good agreement with previously reported values 11,12 and the increases observed on co-ordination (Table 1)

TABLE 1

Infrared	stretching	vibrations	(cm1)
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Complex	$\nu(C\equiv N)$ or $\nu(C=O)$	v(M-X)
CH _s CN	2249	
ThČl ₄ ,4CH ₃ CN	2273	256
UCl ₄ ,4CH ₃ ČN	2278	262
$ThBr_4, 4CH_8CN$	2273	188
UBr ₄ ,4CH ₃ ČN	2276	193
DMA	1647	
ThBr ₄ ,4DMA	1613	176
UBr. 4DMA	1613	180

Complex	$v(C\equiv N)$ or $v(C=O)$	v(U=O)
$UO_{2}Cl_{2}, H_{2}O$ UO_{Cl_{0}, CH_{0}CN}	2280	958 962
UO ₂ Cl ₂ ,2DMA	1613 {	924 918
UO ₂ Br ₂ ,2DMA	1608	922

ThBr₄,4CH₃CN and ThI₄,4CH₃CN, respectively, it has been suggested ¹⁰ that uranium tetrachloride forms the compound UCl₄,2CH₃CN under similar conditions. In addition, the methyl cyanide and NN-dimethylacetamide complexes of uranyl chloride and uranyl bromide have been investigated and we now report the preparation and some properties of the methyl cyanide complexes MX₄,4CH₃CN and UO₂Cl₂,CH₃CN, and the NN-dimethylacetamide complexes, MBr4,4DMA and UO_2X_2 , 2DMA (M = Th and U; X = Cl and Br).

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- 1964, 2527. K. W. Bagnall, A. M. Deane, T. Markin, P. S. Robinson, and
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lie between 24 and 29 cm.⁻¹. The C=N stretching vibration is a single, very sharp, intense peak in each case; a second sharp peak (at 2289 cm.⁻¹ in the free ligand), which has been assigned either to a combination band 13 or to an overtone 14 is observed close to the C=N band, at about 2305 cm.⁻¹, in all the spectra. The thorium- and uranium-halogen stretching vibrations (Table 1) occur around 260 cm.⁻¹ (metal-chlorine) and

⁷ K. W. Bagnall, D. Brown, P. J. Jones, and J. G. H. du Preez, J. Chem. Soc. (A), 1966, 737. ⁸ R. C. Young, J. Amer. Chem. Soc., 1935, **57**, 997. ⁹ K. W. Bagnall, D. Brown, P. J. Jones, and J. G. H. du

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¹¹ M. W. Duckworth, G. W. A. Fowles, and R. A. Hoodless, J. Chem. Soc., 1963, 5665. ¹² H. J. Coerver and C. Curran, J. Amer. Chem. Soc., 1958, **80**,

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190 cm.⁻¹ (metal-bromine), positions which are very similar to those observed for the hexahalogeno-complexes, which can be conveniently prepared ¹⁵ from the methyl cyanide complexes. The co-ordinated methyl cyanide is readily replaced ⁷ by oxygen donor ligands containing the phosphine oxide and sulphoxide groups and the tetrabromide-methyl cyanide complexes also react with excess of DMA in acetone to form the soluble complexes ThBr₄,4DMA and UBr₄,4DMA which precipitate in an impure state as oils on the addition of isopentane to the acetone solution. The pure complexes are obtained by recrystallisation from acetone; for ThBr₄,4DMA it is necessary to have 10% excess of DMA present during recrystallisation to prevent the formation of ligand-deficient complexes, ThBr₄, xDMA (x = 3.6— 3.8). Similar behaviour is observed ¹ for the tetrachloride complex, ThCl₄,4DMA. Like the latter, the thorium and uranium tetrabromide-DMA complexes are hygroscopic; they dissolve in acetone, methyl cyanide, alcohol, nitromethane, and ether, but are insoluble in non-polar solvents such as benzene, ethyl acetate, carbon tetrachloride, and isopentane. Conductivity measurements show that these compounds, like the tetrachloride-DMA complexes, are virtually non-electrolytes in nitromethane, Λ_{500} and Λ_{1000} being 42.6 and 45.0 mhos for ThBr₄,4DMA and 26.3 and 27.4 mhos for the uranium tetrabromide complex. The infrared spectra of the complexes between 5000 and 666 cm.⁻¹ are almost identical with those reported previously 1,5 for the tetrachloride-DMA complexes with a negative shift of 34 cm.⁻¹ for the carbonyl stretching frequency compared with ¹ 44 cm.⁻¹ for ThCl₄,4DMA and ⁵ only 29 cm.⁻¹ for UCl₄,2.5DMA. The metal-bromine stretching frequency, v_3 , occurs at approximately 180 cm.⁻¹, slightly lower than in the methyl cyanide complexes and ¹⁵ the hexabromo-thorates(IV) and -uranates(IV). When it is heated in a vacuum ThBr₄,4DMA loses DMA above 55° forming ThBr₄,2DMA, stable between 180 and 220°, which decomposes at higher temperatures to a mixture of thorium tetrabromide and the dioxide.

Magnetic susceptibility results for the uranium(IV) complexes are in Table 2. Although the tetrabromide-

TABLE 2

Magnetic susceptibilities of the uranium(IV) complexes $(\chi_{\rm M} \times 10^6 \text{ c.g.s. units}; T \text{ in }^{\circ} \text{K})$

UCl ₄ ,4	UCl ₄ ,4CH ₃ CN UBr ₄ ,4CH ₃ CN		CH3CN	UBr ₄ ,4DMA		
Т	χм	Т	χж	Т	χ _M	
306	3248	303	3405	293	3287	
296	3374	258	3819	257	3458	
257	3743	215	4211	215	3718	
216	4111	175	4729	179	3886	
177	4645	138	5421	156	4024	
139	5256	108	6170	134	4132	
109	5829			102	4315	

and tetrachloride-methyl cyanide complexes appear to exhibit Curie-Weiss dependence between 100 and 300°K, with moderately large Weiss constants, -130 and -140°

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respectively, the resultant magnetic moments, 3.46 and 3.44 B.M., respectively, can have little significance. The room-temperature magnetic susceptibility of the tetrabromide complex is slightly larger (ca. 3%) than that of UCl₄,4CH₃CN (Table 2) but this difference is not as great as that observed for the hexamethylphosphoramide complexes 7 UX4,2HMPA and the hexahalogenosalts ¹⁶ (Ph₃PH)₂UX₆ (X = Cl and Br). The magnetic susceptibility of the uranium tetrabromide-DMA complex also exhibits Curie-Weiss dependence over the above temperature range but such dependence is relatively slight and the large value of θ , the Weiss constant, -550° , renders the value of the resultant magnetic moment, 4.72 B.M., virtually meaningless.

Uranyl Halide Complexes.-Uranyl chloride monohydrate, UO₂Cl₂,H₂O, was the starting material for the preparation of the methyl cyanide and dimethylacetamide complexes. We have confirmed that when hydrated uranyl chloride, UO_2Cl_2, xH_2O (x > 6), is heated with thionyl chloride under reflux 17 it is converted into the monohydrate UO₂Cl₂,H₂O and not into anhydrous uranyl chloride. The bands associated with the O-H stretching vibration and $H^{/}$ H rocking mode occur at 3425 and 1603 cm.⁻¹, respectively, in the infrared spectrum of the monohydrate, so it is unlikely that this compound can be formulated as H₂UO₃Cl₂ as suggested.¹⁸ Other infrared results are listed in Table 1. Treatment of UO₂Cl₂,H₂O with methyl cyanide at room temperature results in replacement of the co-ordinated water by methyl cyanide and the pale yellow, slightly soluble, solid 1:1 complex, UO₂Cl₂,CH₃CN, is obtained. Both the monohydrate and the methyl cyanide complex react with DMA in acetone to form an intensely yellow solution from which an oil precipitates on the addition of ethyl acetate. The crystalline complex UO₂Cl₂,2DMA is obtained by dissolving this oil in acetone, reprecipitating the oil with ethyl acetate, and washing the product with cold acetone. The corresponding uranyl bromide-DMA complex, UO₂Br₂,2DMA, has been obtained from a solution of uranyl bromide in anhydrous methyl cyanide, prepared ¹⁹ by the successive metatheses:

$$UO_{2}CI_{2},H_{2}O + 2AgCIO_{4} \longrightarrow UO_{2}(CIO_{4})_{2} + 2AgCI \downarrow$$
(1)
$$UO_{2}(CIO_{4})_{2} + 2LiBr \longrightarrow UO_{2}Br_{2} + 2LiCIO_{3} \downarrow$$
(2)

The hygroscopic uranyl chloride-methyl cyanide complex is readily soluble in acetone, nitromethane, methylene dichloride, and alcohol but insoluble in benzene, carbon tetrachloride, and isopentane. It is only moderately soluble in anhydrous methyl cyanide and the high solubility reported 19 for uranyl chloride in methyl cyanide is presumably due to the presence of water in the solvent. The uranyl chloride-DMA complex, which is quite stable in the atmosphere, is insoluble in acetone, ethyl acetate, alcohol, ether, isopentane, methylene dichloride, and benzene, is slightly soluble in

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 ¹⁸ J. Prigent and I. Lucas, *Compt. rend.*, 1961, 253, 474.
 ¹⁹ J. P. Day, Thesis, Oxford, 1965.

¹⁵ D. Brown, J. Chem. Soc. (A), 1966, 766.

¹⁶ J. P. Day and L. M. Venanzi, J. Chem. Soc. (A), 1966, 197.

methyl cyanide and nitromethane, and dissolves readily in excess of ligand. The uranyl bromide-DMA complex exhibits similar solubilities apart from being slightly soluble in acetone and alcohol.

The main features of the infrared spectra of these uranyl complexes are summarised in Table 1. The $C\equiv N$ stretching vibration shifts by about 30 cm.⁻¹ on co-ordination of methyl cyanide to uranyl chloride and the C=O stretching vibration by about 34 cm.⁻¹ on coordination of NN-dimethylacetamide. The remaining ligand bands in the spectra of the DMA complexes between 5000 and 303 cm.⁻¹ are again virtually identical with those of the tetrachloride complex UCl_{4} , 2.5DMA. More interesting, however, is the appreciable change in the position of the uranyl ion (UO_2^{2+}) symmetric stretching vibration which occurs on replacement of a single water or methyl cyanide molecule by two of dimethylacetamide (Table 1).

Uranyl bromide is appreciably more soluble in methyl cyanide than is the corresponding chloride. We have been unable to prepare a pure uranyl bromide-methyl cyanide complex by evaporation of a solution prepared by the above metatheses. The orange-yellow product invariably contains perchlorate (probably $LiClO_{4}$) which,

TABLE 3

Partial X-ray powder diffraction patterns for the uranyl chloride complexes

$\rm UO_2Cl_2, H_2O$		UO ₂ Cl ₂ ,CH ₃ CN		UO ₂ Cl ₂ ,2DMA		
$\sin^2 \theta$		$\sin^2 \theta$		$\sin^2 \theta$		
(obs.)	I (estd.) *	(obs.)	I (estd.)	(obs.)	I (estd.)	
0.0182	M +	0.0144	S	0.0089	S	
0.0189	W	0.0218	M —	0.0097	S	
0.0200	M +	0.0302	W-	0.0157	S	
0.0261	W-	0.0352	$\mathbf{M} +$	0.0161	w	
0.0280	W-	0.0382	$\mathbf{M} +$	0.0280	$\mathbf{M} +$	
0.0315	W	0.0412	M+	0.0292	W+	
0.0327	S	0.0571	M	0.0351	M	
0.0504	M +	0.0629	\mathbf{M}	0.0364	W	
0.0521	W+	0.0659	W	0.0421	\mathbf{M} +	
0.0649	W+-	0.0728	M —	0.0449	M	
0.0745	M -	0.0844	W	0.0459	W	
0.0791	M —	0.0959	M -	0.0473	м	
0.0863	\mathbf{M}	0.1044	M -	0.0497	W	
0.0903	W+	0.1116	W	0.0521	W+	
0.0925	W	0.1225	W	0.0612	M	
0.1034	W-	0.1363	M -	0.0635	W-	
0.1088	S	0.1414	W-	0.0647	w	
0.1136	Μ	0.1441	M	0.0667	$\mathbf{W}+$	
*	Estimated ·	S strong	· M medir	w w	alz	

Estimated: S, strong; M, medium; W, weak.

although it can be concentrated in solution by washing the initial product with a small volume of anhydrous methyl cyanide, cannot be completely eliminated. The purest samples of the uranyl bromide complex (ca. 3%impurity) contained between 1.5 and 2 molecules of methyl cyanide. The X-ray powder pattern of this material showed a slight resemblance to that of UO₂Cl₂,CH₃CN (Table 3) but the bromide complex was insufficiently crystalline to allow a decision as to whether

²⁰ A. M. Deane, J. Inorg. Nuclear Chem., 1965, 27, 751.
²¹ D. Brown and R. Colton, J. Chem. Soc., 1964, 714.
²² D. Brown and P. J. Jones, J. Chem. Soc. (A), 1966, 733.

they were isostructural. The uranyl chloride- and bromide-DMA complexes on the other hand were highly crystalline and obviously isostructural; the partial X-ray powder pattern of the former is listed in terms of $\sin^2 \theta$ in Table 3 together with similar results for the monohydrate and methyl cyanide complexes UO₂Cl₂,H₂O and UO₂Cl₂,CH₃CN. The results have not yet been interpreted.

EXPERIMENTAL

The moisture-sensitive methyl cyanide and DMA complexes were prepared and handled in a dry-atmosphere box in which samples were prepared for infrared spectra, X-ray powder diffraction, and magnetic susceptibility studies and in which conductivity measurements were performed. X-Ray powder diffraction photographs were obtained on a Debye-Scherrer 19 cm. camera with filtered Cu- K_{α} radiation ($\lambda = 1.54051$ Å). Infrared spectra were recorded on a Hilger H800 spectrometer with sodium chloride and cæsium bromide optics (5000–303 cm.⁻¹) and a vacuum grating instrument (303-125 cm.⁻¹). Samples were mounted as mulls in Nujol or compressed in paraffin wax.²⁰ Magnetic susceptibilities were measured by the Guoy method, on a balance described elsewhere,²¹ with the samples mounted as described previously. The observed susceptibilities were corrected for the diamagnetism of the anions, ligands, and central cation. Thermogravimetry was performed with the balance described recently,²² at a pressure of 10^{-4} mm. Hg. and with a heating rate of 0.6° per min.

Materials.--Uranium and thorium tetrachloride were prepared as described previously; 7 the tetrabromides were prepared from the elements at 600-700° in vacuo and uranyl chloride monohydrate was obtained by refluxing higher hydrates with thionyl chloride. Methyl cyanide was purified and dried as described previously ²³ and stored over molecular sieves; commercial DMA was redistilled before use. Solutions of uranyl bromide in methyl cyanide were obtained by treating uranyl chloride $(1\cdot 3 g.)$ suspended in methyl cyanide (5 ml.) with silver perchlorate (1.5 g.) in methyl cyanide (3 ml.), removing the precipitated AgCl by centrifugation, and adding lithium bromide (0.62 g.) in methyl cyanide (3 ml.) to the supernatant solution of uranyl perchlorate. The precipitated lithium perchlorate was centrifuged off and the supernatant liquid was concentrated to ca. 5 ml. by vacuum evaporation.

Methyl Cyanide Complexes.---Methyl cyanide (5 ml.) was added to the appropriate tetrahalide or to uranyl chloride monohydrate (ca. 2 g.) and the mixture kept at room temperature for a few hours. The resulting solids were isolated by centrifugation and vacuum-dried at room temperature (Table 4).

Tetrabromide-NN-DimethylacetamideComplexes.-The appropriate tetrabromide or the methyl cyanide complex (1 g.) was dissolved in acetone (10 ml.) and excess of DMA (2 ml.) added. The addition of isopentane (20 ml.) precipitated an oil which was redissolved in acetone (5 ml.) and again precipitated by isopentane. Further isopentane washes $(2 \times 20 \text{ ml.})$ induced solidification of the oil and the product was recrystallised from the minimum volume of hot acetone and vacuum-dried at room temperature (yield ca. 70%).

23 K. W. Bagnall, D. Brown, and P. J. Jones, J. Chem. Soc., 1964, 2396.

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Uranyl Chloride-NN-Dimethylacetamide Complex.—Uranyl chloride monohydrate or the methyl cyanide complex (1 g.) was dissolved in acetone (5 ml.) and excess of DMA (1 ml.) added. On the addition of ethyl acetate (20 ml.) an

TABLE 4 Analyses

		Fo	Found (%)		Required (%)		
Compound	Colour	\mathbf{M}	\mathbf{X}	Ν	\mathbf{M}	\mathbf{x}	Ν
ThCl ₄ ,4CH ₃ CN	White	43.1	26.3	10.2	43.1	26.4	10.4
UCl ₄ ,4CH ₃ ČN	Grey-green	44 ·2	26.4	10.1	43 ·8	$26 \cdot 1$	10.3
ThBr ₄ ,4CH ₃ CN	White	32.3	44.3	7.8	$32 \cdot 4$	44.7	7.8
UBr ₄ ,4CH ₃ ČN	Blue-grey	$32 \cdot 9$	44.2	7.6	3 3 ·0	44 ·3	7.8
UO2Cl2,CH3CN	Pale yellow	61.9	18.3	3.7	62.3	18.6	3.7
ThBr ₄ ,4DMA	White	$25 \cdot 6$	$35 \cdot 2$	6.1	$25 \cdot 8$	35.5	$6 \cdot 2$
UBr ₄ ,4DMA	Green	26.1	34.9	6.0	26.3	$35 \cdot 3$	$6 \cdot 2$
UO2Čl2,2DMA	Yellow	46.0	13.8	5.4	46.2	13.8	5.4
UO ₂ Br ₂ ,2DMA	Orange-	39∙6	26.7	4.7	39.4	26.5	4 ·6
	vellow						

M, Metal; X, halide; N, nitrogen.

oil precipitated; this was dissolved in acetone and reprecipitated by ethyl acetate. The complex solidified on

²⁴ A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," Longmans, London, 1953, p. 248. the addition of a further volume of acetone and the *product* was recrystallised from nitromethane and vacuum-dried at room temperature (yield ca. 70%).

Uranyl Bromide-NN-Dimethylacetamide Complex.— Excess of DMA (2 ml.) was added to methyl cyanide (5 ml.) containing uranyl bromide (2 g.) and an oil was precipitated by the addition of acetone (10 ml.) and isopentane (25 ml.). After several cycles involving dissolution in acetone and precipitation by isopentane, the oil was solidified by vacuum evaporation. The *product* was dissolved in the minimum of hot acetone and the complex crystallised by prolonged cooling in ice (yield *ca.* 40%).

Analysis.—Thorium and uranium were weighed as ThO_2 and U_3O_8 , respectively, after ignition of the complexes moistened with aqueous ammonia. Halogen was determined by potentiometric titration against standard silver nitrate solution and nitrogen was determined ²⁴ by the Kjeldahl method.

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