Uranium(IV) Poly(pyrazol-1-yl)borate Complexes

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The uranium(IV) tetrakis[(pyrazol-1-yl)borates], $U[H_nB(pz)_{4-n}]_4$ (pz = $C_3H_3N_2$ and n = 1 or 2), and $[UCl_2\{HB(pz)_3\}_2]$ have been prepared. Some evidence for the formation of $K[UCl_2\{H_2B(pz)_2\}_3]$.thf (thf = tetrahydrofuran) has also been obtained. The ^1H n.m.r., i.r., and electronic spectra of these complexes are discussed.

SINCE the poly(pyrazol-1-yl)borate ligand, $[H_nB(pz)_{4-n}]^-$, was first reported by Trofimenko,[1] a wide variety of Group 2 and *d*-transition-element complexes of the ligand have been described;[2] most of the latter are derived from metals in the oxidation state II. The behaviour of these ligands parallels that of their η-cyclopentadienyl (cp) analogues and recently metallocenes containing both cp and poly(pyrazol-1-yl)borate groups have been reported.[3] Examples of complexes of this ligand with elements in oxidation state IV appear to be unknown, and it was therefore of interest to investigate the formation of uranium(IV) complexes with these ligands and to attempt to ascertain the mode of bonding in the products by ^1H n.m.r. and electronic spectroscopy. The actinoid tetrakis(cyclopentadienyl) complexes are well documented,[4,5] but the corresponding bis(η-cyclopentadienyl)uranium(IV) dichloride[6] is now thought[7] to be ionic of the form $[(cp)_3U]_2[UCl_6]$, so that it was also of interest to attempt to prepare the analogous bis[poly(pyrazol-1-yl)borato]-uranium(IV) dichlorides.

RESULTS AND DISCUSSION

Uranium(IV) *Complexes*.—Pale green uranium(IV) tetrakis[hydrotris(pyrazol-1-yl)- and tetrakis[dihydrobis(pyrazol-1-yl)-borates] were obtained as the thf adducts by reaction of uranium tetrachloride with the stoicheiometric quantity of the potassium salt of the appropriate anion in thf (thf = tetrahydrofuran). In both cases the product remained in the solvent phase from which it was recovered as an oily solid on vacuum evaporation. Solid products were obtained from these materials by trituration with n-pentane; the solvated hydrotris(pyrazol-1-yl)borate complex loses thf when left in contact with n-pentane overnight. Unsolvated products were also obtained by using 1,2-dimethoxyethane (dme) as the solvent for the preparation, but the analyses of the products obtained in this way were less satisfactory.

Unsolvated $[UCl_2\{HB(pz)_3\}_2]$ precipitated as a green solid, together with potassium chloride, when the stoicheiometric quantities of the potassium salt and uranium tetrachloride were mixed in dme. The complex was isolated from the mixture by dissolution in dichloromethane and evaporation of the resulting solution; this solubility suggests that the complex is a molecular species, unlike[7] '$(cp)_2UCl_2$.' In contrast, the reaction of uranium tetrachloride with $K[H_2B(pz)_2]$ in thf under the same conditions at one stage yielded a solution, from which a species of composition $K[UCl_2\{H_2B(pz)_2\}_3]$,thf was isolated as a green solid, together with a precipitate of a green oil mixed with potassium chloride. Later attempts to repeat the preparation yielded only the green oily precipitate which was insoluble in dichloromethane and thf, and which decomposed on contact with acetone. All the poly(pyrazol-1-yl)borate preparations in thf appeared to yield this intractable by-product to some extent. From the stoicheiometry of the reaction the oil may be solvated $K[UCl_4\{H_nB(pz)_{4-n}\}]$, but this was not established conclusively due to the insolubility of the species in the common organic solvents.

Attempted preparation of $[UCl_3\{HB(pz)_3\}]$ from the stoicheiometric quantities of the tetrachloride and $K[HB(pz)_3]$ in dme yielded a solution of the tetrakis complex, $U[HB(pz)_3]_4$, and a precipitate of $[UCl_2\{HB(pz)_3\}_2]$; presumably the crystal energy of the latter is large enough to lead to disproportionation of $[UCl_3\{HB(pz)_3\}]$ in this solvent, if indeed it is formed at all.

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[1] S. Trofimenko, *J. Amer. Chem. Soc.*, 1966, **88**, 1842.

[2] S. Trofimenko, *Chem. Rev.*, 1972, **72**, 497.

[3] D. J. O'Sullivan and F. J. Labor, *J. Organometallic Chem.*, 1973, **57**, C58.

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[5] K. W. Bagnall, 'The Actinide Elements,' Elsevier, Amsterdam, 1972, p. 232.

[6] P. Zanella, S. Faleschini, L. Doretti, and G. Faraglia, *J. Organometallic Chem.*, 1971, **26**, 353.

[7] B. Kanellakopulos, C. Aderhold, and E. Dornberger, *J. Organometallic Chem.*, 1974, **66**, 447.

These complexes are much more stable towards air and moisture than are the known uranium(IV) cp analogues, but even so they decompose quite rapidly on exposure to air, both in the solid state and in dry non-aqueous solvents. However, the solids can be stored for some weeks in a dry nitrogen atmosphere of low (*ca.* 40 p.p.m.) oxygen content. The complexes $U[HB(pz)_3]_4$, $U[H_2B(pz)_2]_4$,thf, and $[UCl_2\{HB(pz)_3\}_2]$ are soluble in dichloromethane and dimethyl sulphoxide (dmso); the tetrakis complexes are also soluble in acetone, benzene, dme, and thf. All are insoluble in aliphatic hydrocarbons, and are decomposed by chloroform, with the separation of white gelatinous products of unknown composition. The complex $[UCl_2\{HB(pz)_3\}_2]$ appears to decompose in a similar manner in contact with acetone or benzene. All three complexes dissolve in nitromethane with some oxidation to uranium(VI). Preliminary work indicates that complexes of the type $[(cp)_nU\{H_xB(pz)_{4-x}\}_{4-n}]$ may result from the reaction of $[(cp)_3UCl]$ or '$(cp)_2UCl_2$' with $K[H_xB(pz)_{4-x}]$; this is being further investigated.

^{1}H *N.M.R. Spectra.*—The ^{1}H n.m.r. spectra of the tetrakis complexes and of $[UCl_2\{HB(pz)_3\}_2]$ were recorded using $(D_3C)_2SO$ and CD_2Cl_2 as solvents. In all cases the assignments were made using the integral data and by employing the double-resonance technique; in some instances the integrals were inadequate and the peaks were cut out and weighed. All resonances, unless stated otherwise, are relative to $SiMe_4$ as external standard. The spectra of the potassium salts used for the preparation have been reported by Trofimenko.[8]

Very large displacements of the resonances were observed, as expected for complexes containing a paramagnetic metal ion; the line shapes were broad, indicating large electron-spin relaxation times, unlike the line shapes observed in the ^{1}H n.m.r. spectra of cyclopentadienyluranium(IV) alkyls or aryls.[9] Theoretical calculations for these uranium(IV) cp complexes indicate [9] that where the Lande factor, g_j, is greater than unity, as is the case for uranium(IV) species, downfield shifts should be observed. This is reported [10] to be the case for alkoxides of the type $[(cp)_3U(OR)]$, although in the (cyclopentadienyl) uranium(IV) alkyls this was only observed for protons bonded to an α-carbon atom. Downfield shifts were observed in the ^{1}H n.m.r. spectra of all the uranium(IV) poly(pyrazol-1-yl)borates examined in this work.

$[UCl_2\{HB(pz)_3\}_2]$. The spectrum in CD_2Cl_2 exhibited six resonances (Table 1); spin decoupling of the 409 Hz resonance, which split the resonance of 754 Hz into a doublet with pronounced asymmetry to high field, indicated the need for a downfield scan. This led to the discovery of the resonance at 2 130 Hz. From the scale expansion of the spectrum it is clear that the 754 Hz resonance is a triplet and that at 409 Hz is a doublet, although in both cases the coupling constants could not be obtained accurately. Spin decoupling also indicated that the protons which gave rise to the resonances at 656 and 815 Hz were coupled.

TABLE 1

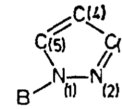
Proton chemical shifts (Hz) *

	$[UCl_2\{HB(pz)_3\}_2]$		$U[H_2B(pz)_2]_4$,-thf
Assignment †	CD_2Cl_2	$(D_3C)_2SO$	CD_2Cl_2
H(3) (b)	2 130 (4)		
H(3), H(5) (n)	815 (4)	742 (4), d	
H(3), H(5) (b)		713 706 704 695 } (8), sm	788 (16)
H(4) (b)	754 (4), t	582 (4), t	646 (8)
H(4) (n)	656 (2)	609 (2), t	
H(5) (b)	409 (4), d		
B–H	148 (2)	269 (2), s	144 (2), 810 (4), 1 346 (2)

s = Singlet, d = doublet, t = triplet, m = multiplet, and sm = sharp multiplet.

* Proton integration is given in parentheses. † (b) and (n) refer to pyrazolyl groups which are bonded or not bonded, respectively, to the uranium atom.

The solid reflectance spectrum (400—2 100 nm) of the complex is characteristic of six-co-ordinate uranium(IV), which indicates that the $[HB(pz)_3]^-$ group is behaving as a bidentate and not a tridentate ligand. The ^{1}H n.m.r. spectrum can be assigned on this basis; the 2 130 Hz resonance is due to the C(3) proton in four of the six pyrazolyl groups, that is, those nearest to the nitrogen atom, N(2), bonded to the paramagnetic uranium atom, so giving rise to the very large contact shift. The triplet at 754 Hz and doublet at 409 Hz are due to the C(4) and C(5) protons respectively of the same four pyrazolyl groups. If this assignment is correct then the C(3) and C(4) protons are influenced by the uranium atom respectively *via* C(3), N(2), and C(4), C(3), N(2), while the C(5) proton is influenced *via* C(5), N(1) by the boron atom, so accounting for the downfield shifts that are observed. The single resonance at 815 Hz is due to the four C(3) and C(5) protons of the remaining two pyrazolyl groups, neither of which are bonded to the uranium atom, and the resonance at 656 Hz is due to the two C(4) protons in these pyrazolyl groups. This leaves the broad resonance at 148 Hz, equivalent to two protons, which can be assigned to the two terminal protons bonded to the boron atom. At −2 °C the four predominant resonances in the spectrum became broader and shifted downfield with respect to the 2 130 Hz resonance, taking the position of the latter to be constant, the change being reversed on warming to 33 °C.



Because of the low b.p. of CD_2Cl_2, the effect of temperature on the C(3) proton resonance was examined

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[8] S. Trofimenko, *J. Amer. Chem. Soc.*, 1969, **91**, 588.

[9] T. J. Marks, A. M. Seyam, and J. R. Kolb, *J. Amer. Chem. Soc.*, 1973, **95**, 5529.

[10] R. von Ammon, R. D. Fischer, and B. Kanellakopulos, *Chem. Ber.*, 1972, **105**, 45.

using tetrachloroethane as solvent. This resonance appeared at 2 033 Hz at room temperature, but the peak broadened and moved to 1 867 at 61, 1 733 at 88, and 1 591 Hz at 127 °C, with full width at half maximum values of 5, 12, 14, and 15 Hz respectively. This probably indicates that at these higher temperatures the pyrazolyl groups are becoming equivalent since on return to room temperature the resonance returns to 2 033 Hz, indicating that decomposition does not occur at 127 °C.

The ^{1}H n.m.r. spectrum of the complex in $(D_3C)_2SO$ (Table 1) differed markedly from that in CD_2Cl_2, although spin decoupling showed that the protons at 609 and 742 Hz are coupled, as are those at 582 Hz with the multiplet at 700 Hz, indicating that the (pyrazol-1-yl)borate group is still acting as a bidentate ligand. Trofimenko[2] reported that donor solvents affect the C(3) proton in the ligand, causing a shift in the resonance, as occurs in this instance, but the complete disappearance of the 2 130 Hz resonance on addition of $(D_3C)_2SO$ to a solution of the complex in CD_2Cl_2, and in $(D_3C)_2SO$ alone, suggests that the changes are due to co-ordination of the solvent to the metal atom. The electronic spectrum of the complex in dmso is still characteristic of six-co-ordinate uranium(IV), but the complex behaves as a weak electrolyte in this medium so that it is possible that the solvent has displaced chloride ion from the complex. If this has occurred, the co-ordinated ligand presumably prevents close approach of the C(3) proton to the metal atom.

$U[H_2B(pz)_2]_4$,thf. The spectrum of this complex in CD_2Cl_2 (Table 1) exhibited resonances due to the ligand protons at 810, 788, 646, and 144 Hz, while those due to the thf protons were at 382 and 196 Hz. Spin decoupling showed that the protons resonating at 646 and 788 Hz were coupled; the integrals of these resonances were in the ratio of 1 : 2 and they are assigned to the C(3) and C(5) protons (788 Hz) and C(4) protons (646 Hz). The ring protons nearest to the uranium atom, unlike those in $[UCl_2\{HB(pz)_3\}_2]$, are unaffected by their proximity to the paramagnetic centre, possibly because of steric hindrance in the more crowded tetrakis complex. It was more difficult to assign the eight protons bonded to the boron atoms; a scan down to 5 000 Hz showed a broad feature at *ca.* 1 340 Hz, and in the high-resolution mode a resonance at 1 346 Hz was detected. Integration in the latter mode was achieved by weighing the appropriate parts of the spectrum, which gave the ratio 1 : 2 : 1 for the resonances at 1 346, 810, and 144 Hz. The integration suggests that in two of the ligand groups there are two boron protons interacting strongly with the uranium atom (1 346 Hz) and two other boron protons that are not interacting (144 Hz). In the two remaining ligand groups there appear to be two equivalent boron protons which are interacting to an appreciable extent with the uranium atom (810 Hz).

The solid reflectance spectrum indicated that the uranium atom is in a low-symmetry environment of high co-ordination number ($\geqslant 8$); it is somewhat similar to the spectrum of[11] $U[NCS]_4$,4dma (dma = *NN*-dimethylacetamide). The $[H_2B(pz)_2]^-$ group evidently acts as a bidentate ligand, but it is not clear whether the thf is co-ordinated since its C–O vibration could not be identified in the i.r. spectrum.

The ^{1}H n.m.r. spectrum in $(D_3C)_2SO$ again differed from that in CD_2Cl_2, although the resonance at 1 346 Hz could still be discerned in the high-resolution mode. The spectrum in this solvent showed a slight upfield shift on heating from 33 to 65 °C, a shift which increased very considerably at 98 °C. The resonance disappeared at 143 °C, presumably due to thermal decomposition of the complex. The effect of added $(D_3C)_2SO$ on the spectrum of the complex in CD_2Cl_2 was followed by recording the spectrum after successive additions of the ligand. After addition of 0·25 volume equivalents the relaxation times of the B–H resonances, and particularly that at 1 346 Hz, decreased markedly, and the resonance at 788 Hz [C(3), C(5) protons] split into two equal-intensity resonances which were 242 and 229 Hz from a CH_2Cl_2 standard as compared with 245 Hz in the absence of $(D_3C)_2SO$. It therefore seems probable that the resonance 229 Hz from the standard is due to the C(3) proton. As further additions of $(D_3C)_2SO$ were made, the relaxation time of the boron protons became shorter and the resonance assigned to the C(3) proton moved closer to the standard until, after addition of one volume equivalent, it was 211 Hz from the standard whereas that due to the C(5) proton was still 242 Hz from the standard. The resonance at 646 Hz split into a well defined triplet as the addition of $(D_3C)_2SO$ proceeded and the coupling constant increased gradually to 20 Hz at 1 volume equivalent added.

$U[HB(pz)_3]_4$. Fluxional behaviour of the pyrazole group in poly(pyrazol-1-yl)borate complexes can be detected[12,13] by temperature-dependent ^{1}H n.m.r. spectroscopy. The ligand $[(pz)B(pz)_3]^-$ forms complexes in which there are three bridging and one terminal pyrazole groups, and it has been shown[12] that in the complex $[\{(pz)B(pz)_3\}Mo(CO)_2(\eta\text{-}CH_2CBrCH_2)]$ the terminal pyrazole group is unaffected by exchange processes and that the ^{1}H n.m.r. line shape is essentially temperature independent. When the terminal pyrazole group is replaced by a proton, the temperature dependence of all the resonances due to the pyrazole groups becomes less marked; this is, apparently, the result of hindered internal rotation about the B–N bond to the terminal pyrazole group. In complexes in which terminal pyrazole groups are present, there is also a large chemical-shift separation of the C(5) proton doublets, a result attributed to the influence of the fourth pyrazole group. Internal rotation is

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[11] K. W. Bagnall, D. Brown, and R. Colton, *J. Chem. Soc.*, 1964, 2527.

[12] P. Meakin, S. Trofimenko, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1972, **94**, 5677.

[13] S. Trofimenko, *J. Amer. Chem. Soc.*, 1969, **91**, 3183.

fast on the n.m.r. time scale and the terminal pyrazole group remains longer in the lower-energy internal-rotation configurations, so that the time-averaged orientations are not isotropic.

The solid reflectance spectrum of $U[HB(pz)_3]_4$ merely indicated that the uranium atom is in an environment of high co-ordination number ($\geqslant 8$) and low symmetry, which does not assist in the assignment of the ^1H n.m.r. spectrum (Table 2). The tentative assignment suggests that the ligand may be bidentate, in which case a terminal proton and a terminal pyrazole group are present in each ligand group. The two sets of doublets at 702, 701 and 695, 692 Hz were coupled to the resonances at 576 and 567 Hz. Following Meakin's [12] approach, the 702 and 695 Hz resonances are assigned to the C(3) protons of the bridging pyrazole groups in slow exchange; similarly the 701 and 692 Hz resonances are assigned to the C(5) protons in the same groups, while those at 576 and 566 Hz are assigned to the C(4) protons in these groups. The resonances assignable to the terminal pyrazolyl group were at 720 [C(3) and C(5) protons] and at 661 Hz [C(4) proton]. Spin decoupling indicated that the resonance at 550 Hz is not coupled to any other proton and it is therefore assigned to the terminal B–H protons. The problem of these assignments can only be resolved satisfactorily by an *X*-ray crystal-structure determination, but all attempts to obtain suitable crystals have failed.

TABLE 2

^1H N.m.r. spectrum of $U[HB(pz)_3]_4$ in CD_2Cl_2

Resonance/Hz	*J*/Hz	Protons
720, bm		8
701 + 702, d	1	16
695 + 692, d	3	
661, d	3	4
576, d	2	8
567, d	2	
550, bm		4

d = Doublet, bm = broad multiplet.

I.R. Spectra.—The i.r. spectra of the uranium complexes were very similar to those observed for other metal poly(pyrazol-1-yl)borates with the characteristic B–H stretching mode appearing at 2 500 cm^{-1}. Due to the large number of bands in their spectra, it was difficult to detect traces of solvent in these complexes. Both thf and, in the case of $[UCl_2\{HB(pz)_3\}_2]$, dme were detected from characteristic resonances at τ 6·17 and 8·03 (thf) or at 6·29 and 6·46 (dme) in the ^1H n.m.r. spectra. The U–Cl stretching mode in the spectrum of $[UCl_2\{HB(pz)_3\}_2]$ appeared at 268 cm^{-1}.

EXPERIMENTAL

All experimental work was carried out in nitrogen-atmosphere dry-boxes because of the hygroscopic nature of uranium tetrachloride and the air and moisture sensitivity of the products. Uranium tetrachloride [14] and the potassium poly(pyrazol-1-yl)borates [15] were prepared by published methods; thf and dme were triply distilled from $Li[AlH_4]$ under a nitrogen atmosphere and stored in the glove-box. Other solvents were dried by published methods [16] and stored over CaH_2 or molecular sieves (type 5A).

Uranium(IV) *Tetrakis*[*dihydrobis*(*pyrazol*-1-*yl*)*borate*]–*Tetrahydrofuran* (1/1).—UCl_4 (1 g, 2·6 mmol) in thf (30 cm^3) was added to $K[H_2B(pz)_2]$ (1·95 g, 10·5 mmol) in the same solvent (5 cm^3) and stirred for 2—3 h. The filtrate from the reaction was evaporated under vacuum and the resulting oily solid was triturated with n-pentane (25 cm^3) to yield the bright green *adduct*, yield 60% {Found: C, 35·7; H, 4·5; N, 24·2; U, 26·5%. $U[H_2B(pz)_2]_4$,thf requires C, 37·4; H, 4·4; N, 25·0; U, 26·5%}. The same procedure with 1,2-dimethoxyethane (dme) as solvent yielded an apparently unsolvated product, but the analyses were less satisfactory {Found: C, 33·2; H, 4·10; N, 27·5; U, 27·1%. $U[H_2B(pz)_2]_4$ requires C, 34·9; H, 3·9; N, 27·1; U, 28·8%}.

Uranium(IV) *Tetrakis*[*hydrotris*(*pyrazol*-1-*yl*)*borate*]–*Tetrahydrofuran* (1/1).—This pale green *complex* was prepared from thf in the same way as $U[H_2B(pz)_2]_4$,thf, yield 60% {Found: C, 40·0; H, 4·15; N, 29·9; U, 20·4%. $U[HB(pz)_3]_4$,thf requires C, 41·2; H, 4·10; N, 29·0; U, 20·5%}. When the adduct was stirred overnight in n-pentane the unsolvated complex was produced {Found: C, 39·6; H, 4·0; N, 29·1; U, 22·1%. $U[HB(pz)_3]_4$ requires C, 39·7; H, 3·7; N, 30·9; U, 21·9%}.

Dichlorobis[*hydrotris*(*pyrazol*-1-*yl*)*borato*]*uranium*(IV).—The pale green *complex* precipitated together with KCl when the stoicheiometric amount of $K[HB(pz)_3]$ in dme was added to UCl_4 suspended in dme. The *product* was extracted from the precipitate into dichloromethane and isolated therefrom by vacuum evaporation, yield 80% {Found: C, 27·6; H, 2·9; Cl, 9·6; N, 22·3; U, 32·4%. $[UCl_2\{HB(pz)_3\}_2]$ requires C, 29·5; H, 2·7; Cl, 9·7; N, 22·7; U, 32·3%}.

Potassium Dichlorotris[*dihydrobis*(*pyrazol*-1-*yl*)*borato*]-*uranate*(IV)–*Tetrahydrofuran* (1/1).—The attempted preparation of $[UCl_2\{H_2B(pz)_2\}_2]$ from thf in some instances resulted in the precipitation of KCl and the formation of a green solution from which the green potassium complex salt was isolated by vacuum evaporation, yield 40% {Found: C, 31·5; H, 4·1; Cl, 8·6; K, 4·2; N, 20·0; U, 28·3. $K[UCl_2\{H_2B(pz)_2\}_3]$,thf requires C, 29·5; H, 3·7; Cl, 8·3; K, 4·5; N, 19·5; U, 27·7%}.

Physical Measurements.—^1H N.m.r. spectra were recorded using a Varian HA-100 100 MHz spectrometer with tetramethylsilane as external standard. Electronic spectra (400—2 000 nm) were recorded using a Beckman DK2a spectrophotometer with samples in solution in 1 cm silica cells or by solid reflectance. I.r. spectra were recorded using a Perkin-Elmer PE 257 spectrometer (4 000—625 cm^{-1}) with samples mounted as mulls in Nujol between NaCl plates. Uranium was determined colorimetrically as the thioglycolate complex; [17] carbon, hydrogen, and nitrogen were determined by combustion, potassium by flame photometry, and chloride by potentiometric titration against silver(I) nitrate.

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[17] M. Hart, personal communication.