Hydrogen-1 Nuclear Magnetic Resonance Study of Uranyl Complexes of Di-2-pyridyl Sulphide and Di-2-pyridyl Ketone

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Hydrogen-1 n.m.r. spectra of uranyl complexes of the ligands (L) di-2-pyridyl sulphide (dps) and di-2-pyridyl ketone (dpk), $[UO_2L_2]X_2$ (X = Cl, ClO_4, NO_3, or NCS), have been run at 250 MHz in the pulsed Fourier-transform mode, and the observed induced shifts for the pyridine-ring protons have been analysed, by means of a computer-assisted method, in terms of the pseudo-contact equation and of the molecular conformation. In general, for protons in *meta* positions with respect to the heteroatom, the shifts observed are essentially dipolar in origin. The pseudo-contact equation in combination with the computer method can be employed to determine the molecular conformation of uranyl complexes in the solution state.

A SMALL number of investigations have been made on the ^{1}H n.m.r. spectra of complexes of uranyl ($[UO_2]^{2+}$) with organic ligands. The magnetic anisotropy of this group was initially proposed as the most important factor determining the observed chemical shifts for the protons of uranyl nitrate adducts.[1-3] More recently, studies on complexes with disubstituted benzenes as ligands [4] have shown that the induced shifts may arise by a dipolar (pseudo-contact) interaction. Other studies on complexes of aromatic amine N-oxides and sulphoxides [5,6] have suggested, however, that deshielding effects arise from drainage of electron density from the donor atom to the metal. It therefore seems that the question of the proton-resonance shifts of complexes of $[UO_2]^{2+}$ is still topical. Furthermore, the determination of the structure of uranyl complexes from n.m.r. data has not attracted much attention. The only investigation, that seemed very promising, was made by Siddall and Steward [7] on complexes of tri-n-butyl

phosphate, trioctylphosphine, and NN-dimethylformamide.

In an earlier paper,[8] details were presented of the preparation and thermal decomposition, and of some i.r. and u.v. spectroscopic studies of the structural properties, of complexes of $[UO_2]^{2+}$ with di-2-pyridyl sulphide (dps) and di-2-pyridyl ketone (dpk) ligands. In the present paper detailed ^{1}H n.m.r. studies on these complexes in solution are discussed. A more general aim of this study is to examine the capabilities of the n.m.r. technique to provide informative data on the metal–ligand interaction as well as useful insights into the stereochemical properties of the complexes. In the present investigation the practical difficulties associated with the very low solubility of the complexes examined were solved by the use of the pulsed Fourier-transform (p.f.t.) method which increased the spectral sensitivity of the ^{1}H resonances to the required order of magnitude. The use of a high-field spectrometer operating at 250 MHz provided a better spectral resolution and large

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[2] C. A. Coulson and G. R. Lester, *J. Chem. Soc.*, 1956, 3650.
[3] T. H. Siddall and C. A. Prohaska, *Inorg. Chem.*, 1965, **4**, 783.
[4] B. Kim, C. Miyake, and S. Imoto, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2015.
[5] M. S. Subramanian and V. K. Manchanda, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3001.

[6] M. S. Subramanian, S. A. Pai, and V. K. Manchanda, *Austral. J. Chem.*, 1973, **26**, 85.
[7] T. H. Siddall and W. E. Steward, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3557.
[8] G. C. Pappalardo and A. Seminara, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1993.

chemical-shift dispersions, which resulted in very simple and readily interpretable spectra even for the complicated second-order systems under study.

EXPERIMENTAL

The complexes of dps, (1)—(4), and dpk, (5)—(8), of the stoicheiometry shown in Table 1, were obtained as described previously.[8]

The ^{1}H n.m.r. spectra were recorded at 20 °C on a Cameca 250 TSN spectrometer operating at 250 MHz in the p.f.t. mode. Total acquisition time was 0.5—1 h, and the number of transients was usually limited to 1 000.

and dpk were retained in the spectra of their complexes with $[UO_2]^{2+}$, assignment of resonances for complexes (1)—(8) was straightforward. Some typical spectra are shown in Figure 1. The precision of the measured chemical shifts was better than 0.01 p.p.m.

RESULTS AND DISCUSSION

The proton spectra obtained are consistent with a single ABMX system which suggests that in the complexes the two pyridine rings of each ligand are in equivalent magnetic environments. This is in accord with the previously proposed[8] structure in which the
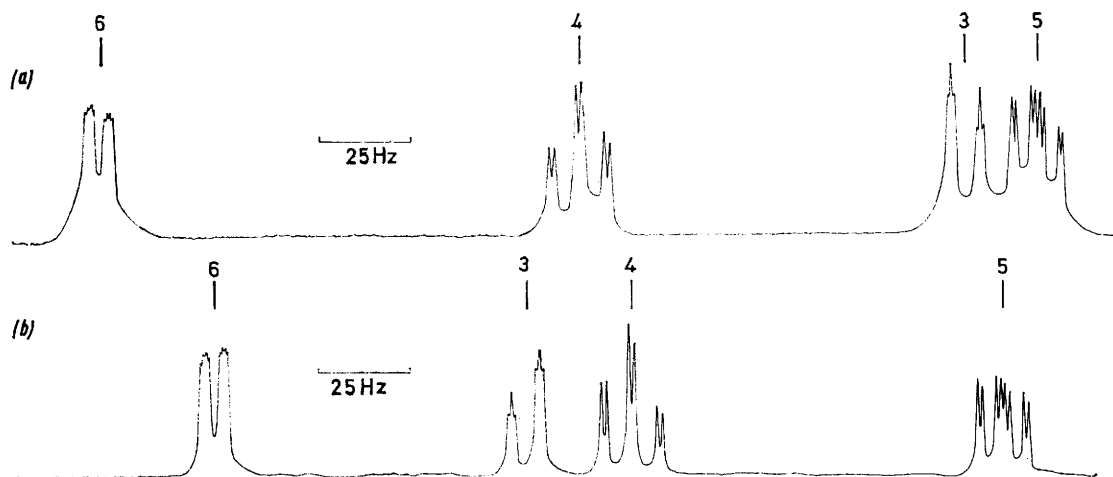

FIGURE 1   The 250-MHz p.f.t. n.m.r. spectra of $[UO_2(dps)_2]Cl_2$ (a) and $[UO_2(dpk)_2]Cl_2$ (b). Frequency markers are centred on the resonance frequencies of the protons indicated. Signal 6 corresponds to 2 201.5 Hz in (a) and to 2 269.1 Hz in (b). In the scale adopted 5 Hz corresponds to 1 cm of the chart abscissa

Complexes (1)—(8) were examined as saturated solutions in nitromethane. All the spectra were recorded relative to internal tetramethylsilane, isotropic shifts of the complexes being calculated with respect to the shifts of the free-ligand protons (in the same solvent, referenced

TABLE 1

Induced shifts (in p.p.m.) for protons of uranyl complexes of dps and dpk. All the values are relative to the resonances of the diamagnetic uncomplexed ligands. The standard numbering scheme in Figure 2 is adopted

Complex	H^3	H^4	H^5	H^6
$[UO_2(dps)_2]Cl_2$ (1)	0.42	0.75	0.73	0.47
$[UO_2(dps)_2][NCS]_2$ (2)	0.26	0.34	0.76	0.36
$[UO_2(dps)][NO_3]_2$ (3)	0.42	0.74	0.73	0.44
$[UO_2(dps)_2][ClO_4]_2$ (4)	1.16	1.12	1.11	0.64
$[UO_2(dpk)_2]Cl_2$ (5)	0.72	0.76	0.74	0.42
$[UO_2(dpk)_2][NCS]_2$ (6)	0.15	0.20	0.19	0.01
$[UO_2(dpk)][NO_3]_2$ (7)	0.53	0.59	0.58	0.26
$[UO_2(dpk)_2][ClO_4]_2$ (8)	0.73	0.76	0.75	0.37

internally to SiMe$_4$). All the complexes examined gave almost first-order spectra at 250 MHz. Spectral analysis for dps was reported earlier;[9] spectral assignment of resonances for dpk was made on the basis of splitting patterns and by using data from previous analyses for pyridine derivatives.[10] Since the spectral patterns of dps

uranium is six-co-ordinate with the dps and dpk ligands locked into a symmetric C_{2v} type conformation. This also indicates that in complexes where the $[UO_2]^{2+}$: L ratio is 1 : 2 the two ligand molecules have coaxial positions.

The induced proton shifts, Δv, of the co-ordinated ligands, obtained from fast-exchange-limit-averaged spectra, are presented in Table 1. Since the stoicheiometry of the complexes is well established, these observed shifts were rationalised using the simplest form of the pseudo-contact equation (1), describing the dipolar

$$\Delta v^{dip} = K(3\cos^2\theta - 1)/r^3 \qquad (1)$$

interaction for an axially symmetric complex.[11,12] In this equation the axial geometric factor $f(r,\theta)$ controls the relative induced shifts, (r,θ) being the polar co-ordinates of the examined nucleus with respect to the principal magnetic axis. (The centre of the $[UO_2]^{2+}$ ion is regarded as a magnetic point-dipole.)

We thus developed a computer search method for placing the magnetic axes and positioning of the $[UO_2]^{2+}$ ion as a best fit to the observed proton-shift data for each complex. Input data consisted in measured Δv

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[10] W. Brugel, *Z. Electrochem.*, 1962, **66**, 159.

[11] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, 1958, **29**, 1361.

[12] R. J. Kurland and B. R. McGarvey, *J. Magnetic Resonance*, 1970, **2**, 286.

values and geometric parameters of the ligand.* By substituting $\Delta\nu$ for $\Delta\nu^{dip}$ values of the ring protons, the constant K in equation (1) was obtained by a least-squares minimisation procedure for each possible value of the geometrical factor. Theoretical values of $\Delta\nu^{dip}$ were thus calculated and compared with $\Delta\nu$, their difference being expressed, for the i nuclei considered, by means of the Hamilton agreement factor (a.f.) given by equation (2). The geometric factors, and thus the

$$\text{a.f.} = [\sum_i (\Delta\nu - \Delta\nu^{dip})^2 / \sum_i (\Delta\nu)^2]^{\frac{1}{2}} \quad (2)$$

$\Delta\nu^{dip}$ values, were evaluated as a function of the two variables ϕ and R; ϕ is the twisting angle about the C(py)–X bonds and R is the distance from the centre of the $[UO_2]^{2+}$ ion to the bonded N atoms of the ligand (see Figure 2). These variables were independently
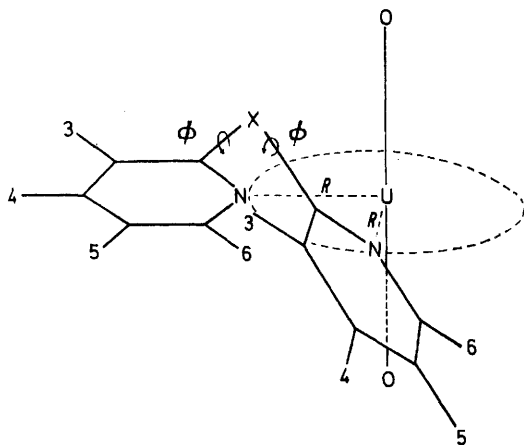

FIGURE 2 Perspective view of the molecular conformation of uranyl complexes of dps (X = S) and dpk (X = CO). A single molecule of ligand in the conformatiom $\phi = 90°$ is shown

varied from 90 to 150° (with a scanning of 5°) and from 2 to 3 Å, respectively.† The range of the possible R values was selected on the basis of X-ray structural data available for the N–U distance in uranyl chelates [15] (mean ca. 2.55 Å). A single R value, as determined by simple trigonometry, is compatible with each ϕ angle; this is because each possible structure of the type shown in Figure 2 must verify the following geometric restrictions: (i) the ligand molecules are arranged around uranium in the ligation plane of the $[UO_2]^{2+}$ ion; (ii) the

* In dps and dpk the pyridine rings were assumed to be regular hexagons, with d(C–C) = d(C–N) = 1.40 Å and d(C–H) = 1.084 Å; bond lengths and valency angles were deduced from structure analyses of bis(p-bromophenyl) sulphide [13] for dps and of benzophenone [14] for dpk. The values of d(C–S) = 1.75 Å, d(C–CO) = 1.50 Å, C–S–C = 109°, and C–CO–C = 122° were adopted in computations.

† The angle ϕ was defined for disrotatory twistings, $i.e.$ of the same magnitude and of opposite sign, of the pyridine rings, starting from the structure $\phi = 0°$ assumed as the one in which the ligand has a planar NN-outside conformation and where the N atoms are turned towards the O–U–O axis. In apposite sub-routine, the program executes computations of r, θ values by means of equations (obtained by trigonometric procedures) which calculate cartesian co-ordinates of each proton as a function of ϕ and R.

N-donor atoms lie in the equatorial plane in Figure 2; (iii) the lone-pair directions point towards the centre of the O–U–O axis.

A first set of calculations was made by assuming dipolar interactions for the protons 3—6. The results obtained indicate that a distinct a.f. minimum occurs for a single ϕ,R combination (reported in Table 2) among those considered. The calculated a.f. values, however, are sizeable, thus suggesting that for some of the four proton resonances the agreement between theoretical $\Delta\nu^{dip}$ and measured $\Delta\nu$ values is poor. The computer-assisted analysis was therefore repeated using in the minimisation procedures three and two resonance signals, successively, all the possible combinations of resonances 3—6 being explored. As shown in Table 2,

TABLE 2

Geometric parameters for uranyl complexes corresponding to a.f. minima. The a.f. values are given as a function of the ring protons considered in the computations (given in parentheses)

			a.f.		
Complex	$\phi/°$	R	(H^3, H^4, H^5, H^6)	(H^3, H^5, H^6)	(H^3, H^5) [a]
(1)	115	2.74	0.516 7	0.381 3	0.015 9
(2)	115	2.74	0.573 0	0.483 5	0.206 9
(3)	115	2.74	0.516 7	0.406 6	0.016 0
(4)	115	2.74	0.571 5	0.532 2	0.217 5
(5)	130	2.19	0.390 8	0.319 8	0.217 8 [b]
(6)	130	2.19	0.616 9	0.598 3	0.115 9 [b]
(7)	130	2.19	0.425 1	0.355 9	0.187 1 [b]
(8)	130	2.19	0.414 2	0.354 9	0.218 0 [b]

[a] For $\phi = 115°$ and $R = 2.74$ except where indicated. [b] $R = 2.72$.

the best refinement of the a.f. values was obtained, in each case, for calculations including protons 3, 5, and 6, and 3 and 5. In fact, a.f. values greater than 0.6 and 0.5 were obtained from calculations involving all the other possible combinations of three and four protons, respectively. The computer outputs showed that, when two instead of four resonance signals were included in the analysis, only for the above proton sets, $i.e.$ 3, 5, and 6, and 3 and 5, did a gradual decrease in a.f. values occur. The procedure thus essentially accomplished, by statistics, the exclusion of all the protons for which a dipolar mechanism is not predominant. At this point it must be mentioned that, in principle, when using data for two proton shifts in the best-fit procedure the solution is obviously underdetermined. However, the solutions quoted in the last column of Table 2 are considered as reliable and valid, in that these were selected among those corresponding to physically acceptable structures. In particular, in order to enable the choice of a single structure for each complex amongst the infinite number of mathematic solutions available, it was assumed that the corresponding ϕ and R values

[13] J. Toussaint, Bull. Soc. chim. belges, 1945, 54, 319.
[14] E. B. Fleischer, N. Sung, and S. Hawkinson, J. Phys. Chem., 1968, 72, 4311.
[15] L. Cattalini, U. Croatto, S. Degetto, and E. Tondello, Inorg. Chim. Acta Rev., 1971, 5, 19.

were of the same order of magnitude as those determined by the analyses carried out with four and three protons.

From results in Table 2, it can be seen that the best agreement with a dipolar mechanism is found for calculations involving the H^3, H^5 pair of resonances. On this basis, it can be concluded that in complexes (1)—(8) the shifts observed for protons 3 and 5 are predominantly dipolar in origin, whereas protons 4 and 6 are deshielded due essentially to drainage of electron density from the ligand to the metal. This conclusion has been previously made by Subramanian et al.[5,6] Furthermore it is also considered that delocalisation of electrons through the π system is responsible for the interactions which occur for the alternate ring protons 4 and 6 that are in ortho and para positions, respectively, with respect to the ligand donor atom. This result also confirms that the above effects in $5f$ systems cannot be neglected even when four bonds separate the nucleus under investigation and the metal centre.

The co-ordination geometry corresponding to the a.f. minima seems acceptable, although the equatorial radii R obtained are a little longer (ca. 0.15 Å) than the average value expected for a $U-N(sp^2)$ bond on the basis of X-ray structure analyses of uranyl–Schiff-base complexes.[15] This difference can be qualitatively accounted for in terms of changes in the geometry of the ligand after co-ordination, as well as by the inherent approximation in the method used. It may be concluded that, as far as the dipolar interactions are concerned, the shifts induced in protons in the co-ordination sphere of the $[UO_2]^{2+}$ ion can be used to obtain information concerning the stereochemistry of uranyl complexes.