Nuclear Magnetic Resonance Spectra of Quinolinolato-complexes of Aluminium, Gallium, and Indium Dialkyls

By **Buddhadev Sen,* Gregory L. White, and J. D. Wander,** Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana 70803, U.S.A.

^{1}H N.m.r. data are presented for a number of novel, organometallic compounds of the form R_2MQ (R = Me, Et, or Bu^i; M = Al, Ga, or In; Q = the anion of quinolin-8-ol). Variations in the chemical shifts of the alkyl protons are rationalized in terms of the opposition of two effects, the first being inductive redistribution of electron density, and the second being the diamagnetic anisotropy of induced electronic circulation in the π-system of the ligand Q; the latter effect causes magnetic non-equivalence in the diastereotopic protons of the isobutyl groups of Bu^i_2AlQ, but the increased inner electron density of the metal atom produces attenuation of this separation for M = Ga, and apparent annihilation of it for M = In. Anisotropic circulation of electrons in the N–M–O portion of the complexes is proposed to explain apparently anomalous chemical shifts of the protons adjacent to the heteroatoms in the aromatic ligand.

WE have reported the preparation and characterization of diethyl(quinolinolato)gallium [1] and we now report a series of compounds of the general formula R_2MQ (R = Me, Et, or Bu^i; M = Al, Ga, or In, and Q = quinolin-8-olate anion). These compounds have been characterized by elemental analysis, molecular-weight determination, and i.r., mass, and n.m.r. spectroscopy. We present here the n.m.r. spectra of these compounds; details of synthesis, and the results of other studies will be published elsewhere.

In these yellow crystalline compounds the metal is four-co-ordinate and has tetrahedral geometry; the quinolin-8-olate anion functions as a bidentate ligand *via* its nitrogen and oxygen atoms.

EXPERIMENTAL

Compared to many other co-ordination compounds of aluminium, gallium, and indium alkyls, the compounds R_2MQ are considerably more stable towards air and moisture, although not indefinitely so. Accordingly, solutions were prepared and transferred into sealed n.m.r. tubes in an inert atmosphere dry box. Spectra were recorded with Varian A60A and HA100 spectrometers at the ambient temperature of the probes (35°), and are referenced to internal Me_4Si.

RESULTS AND DISCUSSION

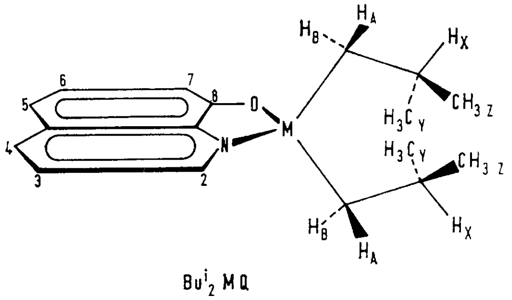
Assignment of free metal alkyl proton resonances was straightforward, because of the first-order splitting pattern; the coupling constants (7 Hz) remained constant throughout the series. The values of the chemical shifts given in Table 1 correspond to the centres of gravity of the multiplets. It was not possible to obtain the n.m.r. spectrum of both the alkyl and the quinolin-8-olate regions of every R_2MQ complex, because of the inadequate solubility of some of the compounds. As in the case of the metal alkyls, R_3M, assignment of the alkyl proton resonance of R_2MQ was generally accomplished on a first-order basis.

TABLE 1

Chemical shifts of alkyl protons of R_3M and R_2MQ in benzene

Compound	Chemical shift (δ) CH$_3$	CH$_2$	CH
Me_2AlQ	-0.95 [a,b]		
Me_3Al	-0.36		
Et_2AlQ	1·33 [a]	0·78 [a]	
Et_3Al	1·09	0·29	
Bu^i_2AlQ	0·75, 0·85	0·35, 0·47 [c]	1·73
Bu^i_3Al	0·98	0·30	1·94
Et_2GaQ	1·22	0·83	
Et_3Ga	1·16	0·54	
Bu^i_2GaQ	1·07, 1·08	0·83	2·07
Bu^i_3Ga	0·95	0·80	2·10
Bu^i_2InQ	1·11	1·22	2·23
Bu^i_3In	1·02	0·80	2·22

[a] Measured at 60 MHz. [b] Hexamethylphosphorictriamide was the solvent for this determination. [c] Determined by ABX analysis.



Bu^i_2MQ

FIGURE 1

The only exception was Bu^i_2AlQ, which gave an eight line AB(X) pattern for the methylene protons. The ABX pattern results from the magnetic non-equivalence of the diastereotopic methylene protons, H_A and H_B (*cf.* Figure 1) of each isobutyl group, which causes each of the nonequivalent methylene protons to couple with the other, as well as with the methine proton, H_X. The *gem*-dimethyl groups designated H_3C_Y and H_3C_Z are also magnetically nonequivalent, and resonate at different fields [Figure 2(b), Table 1]. In the reproduction of the alkyl portion of the spectrum of Bu^i_2AlQ [Figure 2(b)], the methine proton resonance is observed as a low-intensity, seven line pattern; in principle, the methine proton should produce more than seven lines, but the intensities of the remainder

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[1] B. Sen and G. White, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 79.

of these lines are so low that they are not detected. The coupling constants and the chemical shifts of the methyl protons of Bu$^{i}_{2}$AlQ can be obtained directly from the spectrum; in the case of the methylene protons, however, the coupling constants (J_{AX},J_{BX}) and the chemical shifts of H_A and H_B must be calculated. The calculations [2] are accomplished by segregating the eight-line AB pattern into two, four-line AB subspectra, solving the subspectra for apparent resonance positions and manipulating the apparent chemical shifts to generate true values of δ_A, δ_B, J_{AX}, and J_{BX}; J_{AB} is measured directly.

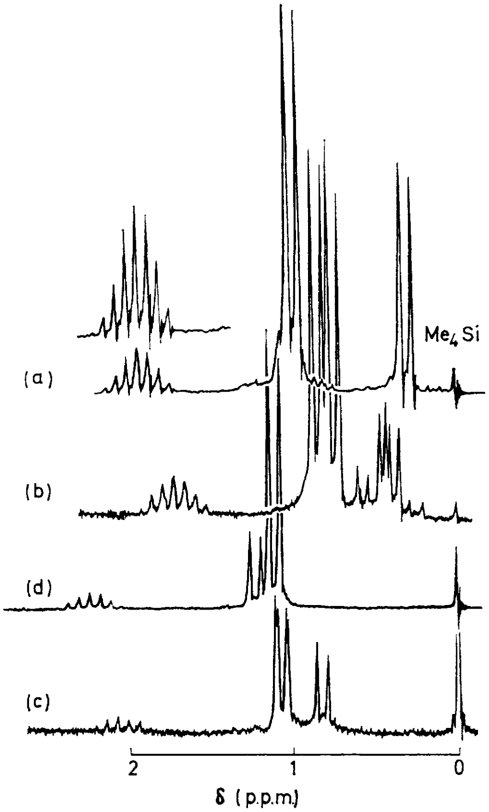

FIGURE 2 High-field portion of the n.m.r. spectra of (a) Bu$^{i}_{3}$Al; (b) Bu$^{i}_{2}$AlQ; (c) Bu$^{i}_{2}$GaQ; (d) Bu$^{i}_{2}$InQ

Bu$^{i}_{2}$GaQ also exhibits magnetic nonequivalence in its n.m.r. spectrum [see Figure 2(c), Table 1]. The two methyl groups of each isobutyl group apparently experience only slightly different magnetic environments, because two doublets are observed for the methyl groups, although the degree of nonequivalence is much diminished in Bu$^{i}_{2}$GaQ; the centres of the methyl doublets of Bu$^{i}_{2}$GaQ are separated by 0·01 p.p.m., whereas for the corresponding signals of Bu$^{i}_{2}$AlQ the separation is 0·1 p.p.m. No evidence of magnetic nonequivalence is seen in the spectrum of Bu$^{i}_{2}$InQ [Figure 2(d)]. In a magnetic field of sufficient magnitude, however, nonequivalence would presumably be exhibited by the *gem*-dimethyl groups of Bu$^{i}_{2}$InQ, and by the methylene protons of both the latter complexes.

The difference in the resonance positions of the non-equivalent protons presumably arises from non-identical interactions of the protons thus related with the diamagnetic anisotropy produced by the circulation of electrons [3] in the π-system of the Q-ligand. The increase in electron population around the metal atom as one descends group IIIA serves to produce more effective screening of the alkyl protons, and, thus, to attenuate the shielding differential between the pairs of proton resonances in question.

Examination of Figures 2(b)—(d) and the data of Table 1 reveals a pronounced deshielding, increasing with increasing atomic number, of the α-alkyl proton resonance of R_2MQ relative to the corresponding signal in the n.m.r. spectrum of R_3M.* The difference in inductive effect between a covalent oxygen–metal bond (in R_2MQ) and the third carbon-metal bond of R_3M is sufficient to account for the downfield position of the α-alkyl proton resonances of R_2MQ. The enhanced nuclear shielding efficiency of the heavier Group IIIA metal atoms suggests greater polarizability of the outer electrons; the increasing relative shift of the α alkyl protons of R_2MQ *vs.* R_3M with increasing atomic number of M parallels and appears to relate to the availability of these outer electrons for delocalization towards Q. The relative shifts of the other alkyl protons appear to reflect the opposition of two effects, (*a*) deshielding that results from inductive displacement of electron density toward the metal atom, and which thus, tends to increase with increasing atomic number, and (*b*) shielding resulting from anisotropic electronic circulation in the ligand π-system. The latter effect falls off somewhat due to the slight increase in bond lengths about the metal atom with increasing atomic number, but more drastic attenuation appears to be provided by the intervening, inner electrons of M, which increase in density significantly between Al and Ga, and again between Ga and In.

The n.m.r. spectra are rather more complex in the low-field region, and it seemed expedient to examine first the spectrum of quinolin-8-ol (HQ) in order to provide a basis upon which to evaluate shifts in the aromatic ligand signals. In the spectrum of HQ, the OH (δ 9·10 p.p.m., broad peak) and H-2 (δ 8·50 p.p.m., narrow doublet of wide doublets) resonances are recognized by their shape and by their occurrence at lowest field; 3-H (δ 6·74 p.p.m.) and 4-H (δ 7·51 p.p.m.), originally identified by the spacings they exhibit ($J_{2,3}$ 4·0, $J_{3,4}$

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* Me_2AlQ is excluded from this discussion. See Table 1.

[2] N. S. Bhacca, personal communication; alternative formalisms for the solution of the ABX spectrum have been presented: J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High-Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959, p. 132*ff*; J. D. Roberts, 'An Introduction to the Analysis of Spin-Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra,' Benjamin, New York, 1962, p. 71*ff*; R. H. Bible, jun., 'Interpretation of Nuclear Magnetic Resonance Spectra—An Empirical Approach,' Plenum Press, New York, 1965, p. 86*ff*.

[3] R. M. Silverstein and G. C. Bassler, 'Spectrometric Identification of Organic Compounds,' 2nd edn., Wiley, New York, 1967, pp. 116—117.

8·0, $J_{2,4}$ 1·5 Hz), were established positively by double-irradiation experiments. The resonances of 5-H, 6-H, and 7-H are rather obscured by overlapping, but a four-line pattern at highest field of the remaining signals (δ 6·95 p.p.m.) is assigned to 7-H on the basis of anticipated shielding by the adjacent hydroxy-group. The corresponding resonances in the spectra of R_2MQ are sufficiently similar in appearance and field position to allow their identification by inspection; the assignments of the aromatic resonances of Bu^i_2AlQ were verified in a similar decoupling experiment.

From the data of Table 2, one is impressed immediately by the fact that the aromatic regions in the n.m.r. spectra of Et_2GaQ and Bu^i_2GaQ are practically identical, whereas substantial changes of field position are in evidence as one passes down Group IIIA in the series Bu^i_2MQ. Other examples of similar trends in the group IIIA metals are known; Allred–Rochow values,[4a] ionization potentials,[4b] and wavelengths of the R_2MQ ligand–metal charge transfer band in the electronic spectrum [5] all show marked divergences from anticipated behaviour in the species having M = Ga. It is assumed here that the n.m.r. spectral anomalies of R_2GaQ are yet another manifestation of the incompletely understood phenomena dictating the other peculiar properties of Ga compounds.

TABLE 2

100 MHz N.m.r. spectral parameters for the quinolin-8-olato protons of R_2MQ

	Chemical shifts[a]						
Compound	2-H	3-H	4-H	5-H	6-H	7-H	O-H
Quinolin-8-ol	8·50	6·74	7·51	7·05—7·30[b]		6·95	9·10
Bu^i_2AlQ	8·44	6·71	7·46	7·79	7·20	6·85	
Et_2GaQ	7·61	6·53	7·51	7·23—7·33[b]		6·69	
Bu^i_2GaQ	7·68	6·53	7·50	7·20—7·33[b]		6·69	
Bu^i_2InQ	8·25	6·72	7·56	7·28—7·50[b]		6·85	

	Apparent coupling constants[c]					
Compound	$J_{2,3}$	$J_{3,4}$	$J_{2,4}$	$J_{5,6}$	$J_{6,7}$	$J_{5,7}$
Quinolin-8-ol	4·0	8·0	1·5	*d*	6·0	3·0
Bu^i_2AlQ	5·0	8·0	1·5	7·5	8·5	1·0
Et_2GaQ	4·5	8·0	1·5	*d*	8·0	4·5
Bu^i_2GaQ	4·5	8·0	1·5	*d*	6·0	4·0
Bu^i_2InQ	4·5	8·0	1·5	*d*	8·5	4·5

[a] In p.p.m. (δ). [b] Unresolved multiplet. [c] First-order values in Hz. [d] Not determined.

In the n.m.r. spectra of Bu^i_2AlQ and Bu^i_2InQ, 3-H and 4-H resonate at the same field as 3-H and 4-H of the free ligand HQ. This suggests that the π electron density of the pyridine-derived portion of Q is substantially unaltered by the presence of the metal ion. The 5-H resonance of Bu^i_2MQ is, however, deshielded with respect to the analogous proton signal in HQ, indicating depressed electron density at C-5. This can be thought to arise from electron movement toward the metal atom through a d–$p\pi$ overlap between the metal and oxygen atoms. Such an interaction would be substantially more favoured in the case of Al, which has vacant *d* orbitals of optimal size for this interaction.

Replacement of the hydroxy-proton by R_2M does not move the 7-H signal of HQ downfield; further, H-2 of Bu^i_2GaQ is enormously shielded relative to the other H-2 resonances of this study, and H-7 of this compound experiences somewhat greater shielding than the H-7 signal of the In and Al analogues. Arguments based on electronegativity and inductive effects fail to provide an explanation, and it is suggested here that the displacements observed at 2-H and 7-H are to a large extent dictated by the anisotropic circulation of electrons in bonds involving the metal atom and one or both of the heteroatoms. Although the data of the present study do not suffice to permit specification of the exact nature of this effect, this argument, which is formulated by analogy to the well-established [3] diamagnetic anisotropy of carbonyl and phenyl groups, provides a rationalization of the present results that is consistent with established principles.

[1/1405 *Received, August 9th*, 1971]

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[4] (*a*) F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry: A Comprehensive Text,' 2nd edn., Interscience, New York, 1966, p. 103; (*b*) *ibid.*, p. 434.

[5] G. L. White, Ph.D. Dissertation, Louisiana State University, 1971, p. 132.