of the triphenylphosphine ligand and its derivatives in other transition metal complexes.[9,14,17] Moreover, we have noted previously[9] that within limits, which exclude significant interatomic repulsions, there is no particular dihedral angle between adjacent phenyl rings that is favored. In the present case, then, the filling of the vacant octahedral site by a phenyl ring, and in particular by a phenyl hydrogen, is energetically favorable, and there is no geometrical basis for postulating that this is a weak metal–hydrogen interaction similar to those postulated to account for various spectroscopic anomalies in a variety of different compounds (ferrocenyl alcohols,[18] protonated acylferrocenes,[19] cycloheptadienium complexes,[20] and $(CH_2)_3[Mn(CO)_5]_2$[21]). The evidence for such weak metal–hydrogen interactions is extremely tenuous, and it would be worthwhile examining these compounds in the solid state by diffraction methods. One might find no geometrical basis for this weak metal–hydrogen interaction, other than restricted rotation brought about by a preferred geometry (as in the present case). Unfortunately, the ruthenium and osmium compounds of Vaska are only slightly soluble in most solvents, and, of more interest, the dilute solutions rapidly change color. For these reasons little solution spectroscopy has been carried out. It is tempting to postulate, however, that the color change results from the rotation of the phenyl ring, followed by reaction at the unblocked octahedral site. If this has some basis in fact, then it should be difficult, if not impossible, to prepare the ruthenium or osmium compounds with a less rigid phosphorus ligand, such as triethylphosphine. One fact is certain: since the phenyl ring geometry leaves no room for a hydride hydrogen, the structure found here provides corroborative evidence to that of Vaska's from infrared spectra that the compound is not a hydride.

It is obvious that the preferred configuration about Ru in this compound is not trigonal bipyramidal, but is octahedral or possibly square pyramidal. We believe that dichlorotris(triphenylphosphine)ruthenium(II) is a true five-coordinated d^6 complex, but that its stability probably arises from intramolecular blocking of the unused octahedral site by the phenyl ring.[22]

Acknowledgment.—It is a pleasure to acknowledge the cooperation and helpful discussions we have enjoyed with Professor L. Vaska.

[17] J. A. Ibers and S. J. La Placa, *Science*, **145**, 920 (1964).

[18] D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, **82**, 5010 (1960).

[19] H. E. Rubalcava and J. B. Thomson, *Spectrochim. Acta*, **18**, 449 (1962).

[20] A. Davison, W. McFarlane, K. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962).

[21] R. B. King, *J. Am. Chem. Soc.*, **85**, 1922 (1963).

[22] NOTE ADDED IN PROOF.—A. Wojcicki has called our attention to a similar argument given by J. Chatt and A. E. Underhill [*J. Chem. Soc.*, 2088 (1963)]. They present evidence that the Rh(III) (d^6) is five-coordinated in bromodi-1-naphthylbis(diethylphenylphosphine)rhodium(III), and they postulate that the stability of the compound results from the shielding of the electron-deficient metal atom by the bulky ligands.

CONTRIBUTION FROM THE SAVANNAH RIVER LABORATORY,
E. I. DU PONT DE NEMOURS AND COMPANY, AIKEN, SOUTH CAROLINA

Studies of Adducts of Metal Salts with Tetraalkyl Alkyldiphosphonates.[1] I. Proton Magnetic Resonance Spectra of Uranyl Nitrate Adducts of Methylenediphosphonates in $CDCl_3$

BY T. H. SIDDALL, III, AND C. A. PROHASKA

Received July 27, 1964

Proton magnetic resonance data are given for $CDCl_3$ solutions of uranyl nitrate adducts of tetraalkyl methylenediphosphonates. These data are interpreted in terms of the effects on nearby protons of the anisotropic magnetic field from the uranyl group.

Introduction

In previous communications[2,3] it was reported that some of the proton resonances were doubled in certain organophosphorus esters that contain an aromatic radical. It is the purpose of this paper to report a similar phenomenon for $CDCl_3$ solutions of the uranyl nitrate adducts of certain tetraalkyl methylenediphosphonates, $(RO)_2P(=O)CH_2P(=O)(OR)_2$, and to present some of the inferences that may be drawn concerning the structure of these adducts and the cause of the resonance multiplication.

Uranyl nitrate adducts offer an exceptional opportunity for study in that so many of them can be isolated easily as crystalline solids of well-defined composition. It is therefore possible to be assured that there is no excess of free ester in these adducts. The methylenediphosphonates are of special interest be-

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[1] The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

[2] T. H. Siddall, III, and C. A. Prohaska, *J. Am. Chem. Soc.*, **84**, 2502 (1962).

[3] T. H. Siddall, III, and C. A. Prohaska, *ibid.*, **84**, 3467 (1962).

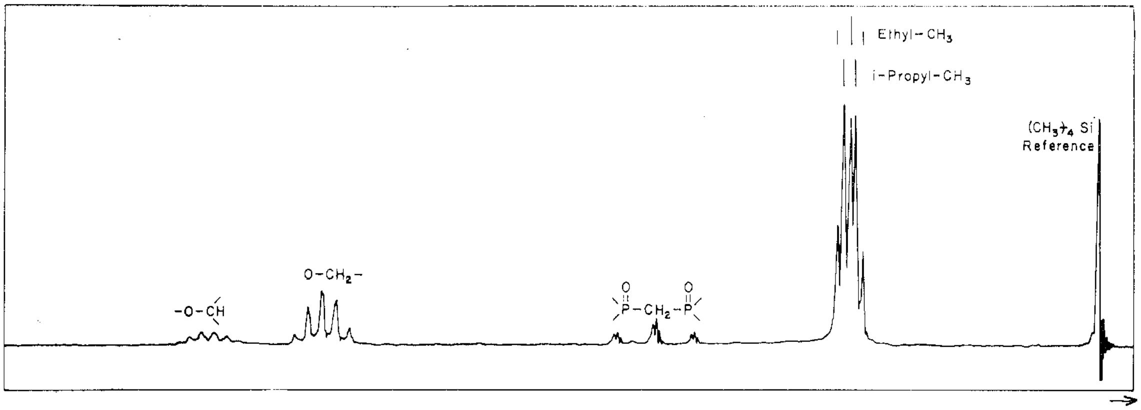

Figure 1.—P.m.r. spectrogram of diethyl di-2-propyl methylenediphosphate (10 vol. % in $CDCl_3$) at 100 Mc.

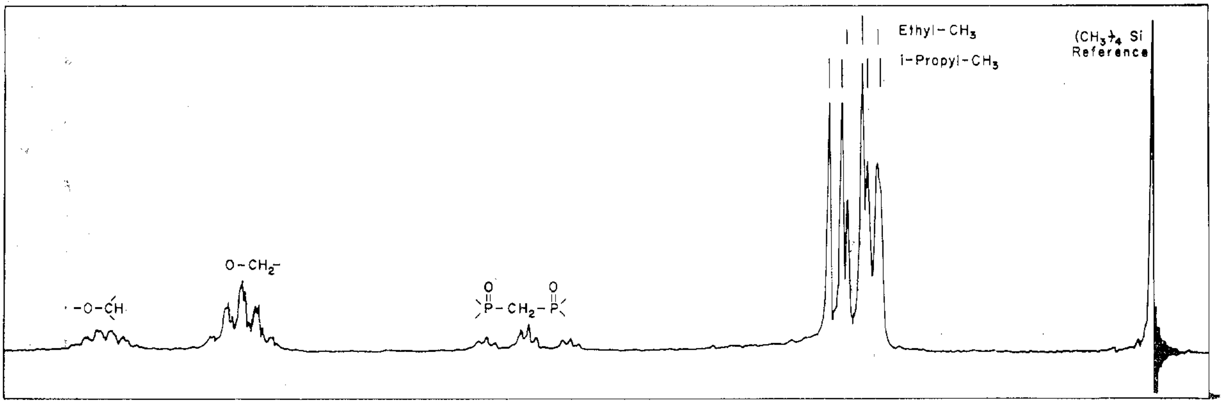

Figure 2.—P.m.r. spectrogram of $UO_2(NO_3)_2$ adduct of diethyl di-2-propyl methylenediphosphate (250 g./l. of $CDCl_3$) at 100 Mc.

cause they combine with uranyl nitrate to form chelates in chloroform solutions. There are nonchelated species of these adducts in the presence of excess methylenediphosphonates or even without excess ester when nonpolar solvents such as CCl_4 are used.

Experimental

The methylenediphosphonates were prepared by three methods, with occasional modifications of these methods as experience was gained. By far the simplest and most direct method was found to be the Arbuzov rearrangement as described by Walmsley and Tyree[4] for the synthesis of tetra-2-propyl methylenediphosphonate. It is to be noted, however, that the tetra-2-propyl methylenediphosphonate prepared in this manner often contains an impurity that can be detected in the proton magnetic resonance spectrum. This impurity is not eliminated by distillation, but is removed by crystallizing the uranyl nitrate adduct.

The yield of tetra-1-alkyl derivatives from the Arbuzov rearrangement is greatly improved, in our experience, by using methylene bromide rather than methylene iodide. Yields of from 40 to 70% of tetraethyl methylenediphosphonate were obtained when methylene bromide was added rapidly to a 50% excess of refluxing triethyl phosphite in a vessel equipped for take-off of ethyl bromide through a 2-ft. Vigreux column. After addition was complete the reaction was held at a bath temperature of 170–180° until evolution of ethyl bromide ceased. Yields of higher 1-alkyl derivatives varied from 25 to 40% when methylene bromide was added slowly to a 50% excess of trialkyl phosphite at a bath temperature of about 170°. The reaction vessel was equipped for take-off through a 2-ft. Vigreux column that was wrapped with heating tape. Column temperature was controlled to allow the take-off rate (by volume) to be roughly twice the addition rate of methylene bromide. After addition was complete, heating was continued until evolution of alkyl bromide ceased.

Diethyl di-2-propyl methylenediphosphonate and the remaining tetra-2-alkyl derivatives, except for 3-methyl-2-butyl, were prepared by the Michaelis reaction in refluxing ethyl ether. Yields were generally only 10–20%. Efforts to improve the yield by operating at lower temperature in ethyl ether or at higher temperature in refluxing methylcyclohexane were not successful. On the other hand, several batches of tetra-*n*-amyl methylenediphosphonate were obtained in 70% yield from the Michaelis reaction in ether.

Tetra(3-methyl-2-butyl)methylenediphosphonate was prepared in 50% yield by esterifying methylenediphosphonic tetrachloride[5] with 50% excess alcohol and pyridine. It was observed that this ester was unstable in contact with alkaline solutions. A very brief contact with dilute sodium carbonate was used for the alkaline wash step that is part of the customary work-up of such esterifications.

All of the diphosphonates were purified by distillation. The butyl and lower alkyl derivatives were purified by ordinary distillation at about 0.3 mm. Higher derivatives were purified by molecular distillation at 1×10^{-4} mm.

The metal nitrate adducts were prepared by adding excess metal nitrate, as the crystalline hydrate, to a 25 vol. % solution of the extractant in a mixture of high-boiling alkanes (Phillips Petroleum Co. Soltrol 170). After shaking for at least 1 hr., the adduct formed as a solid or as a viscous liquid, insoluble in Soltrol 170. The Soltrol 170 was decanted (centrifugation was usually not necessary), and the adduct was dissolved in dichloromethane. This solution was centrifuged, whereupon three phases of the following compositions were usually formed: (1) excess solid metal nitrate; (2) an aqueous phase containing dissolved metal nitrate; and (3) an organic phase containing the adduct. The organic phase was separated from the other two

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[4] J. A. Walmsley and S. Y. Tyree, *Inorg. Chem.*, **2**, 312 (1963).

[5] J. J. Richard, K. E. Burke, J. W. O'Laughlin, and C. V. Banks, *J. Am. Chem. Soc.*, **83**, 1722 (1961).

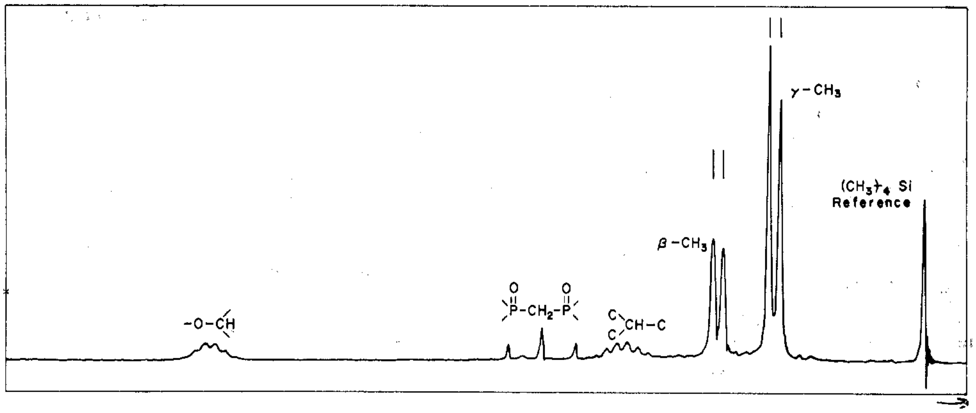

Figure 3.—P.m.r. spectrogram of tetra-2-amyl methylenediphosphate (10 vol. % in $CDCl_3$) at 100 Mc.

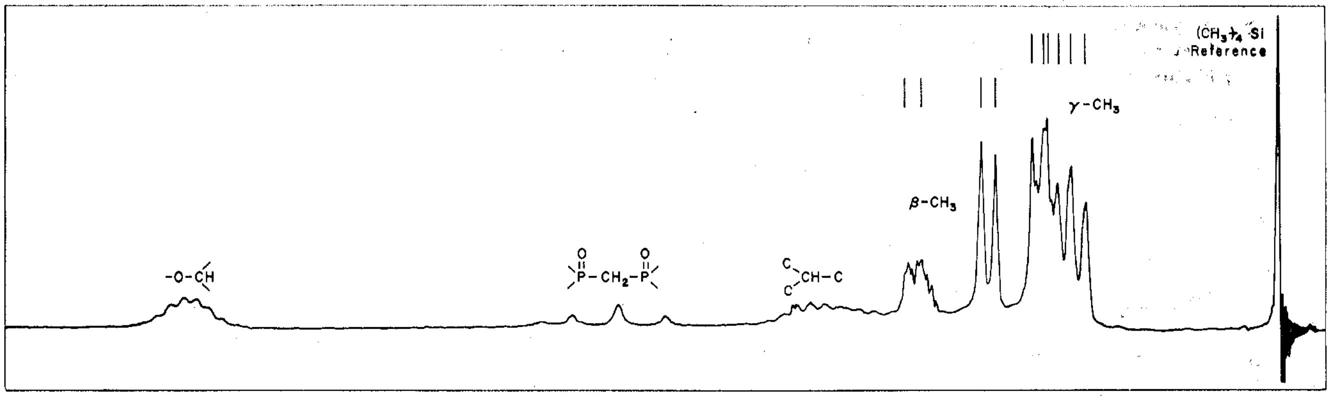

Figure 4.—P.m.r. spectrogram of $UO_2(NO_3)_2$ adduct of tetra-2-amyl methylenediphosphate (250 g./l. of $CDCl_3$) at 100 Mc.

phases, and a mixture of intermediate boiling alkanes (Phillips Petroleum Co. Soltrol 130) was added to it. Dichloromethane was pumped off, with stirring, until the adduct precipitated or formed a separate, viscous liquid phase. The adduct was separated by centrifugation and washed with methylcyclohexane. Next the adduct was redissolved in dichloromethane, and methylcyclohexane was added to the solution. Dichloromethane was again pumped off, with stirring, until the adduct had reprecipitated. The adduct was again separated by centrifugation, washed with petroleum ether, and dried by pumping overnight in a vacuum desiccator.

The measurements of proton resonances were made with a high resolution nuclear magnetic resonance spectrometer, Varian Associates Model 4300 B, at a frequency of 40 Mc., as described previously.[2] The spectra of certain extractants and adducts were also obtained at 60 and 100 Mc. We wish to thank Varian Associates for the use of their A-60 and HR-100 spectrometers, and the personnel of their Pittsburgh Applications Laboratory for assistance in obtaining these spectra.

Molecular weights were determined using a Mecrolab Model 301A vapor pressure osmometer.

Results and Discussion

Figures 1, 2, 3, and 4 illustrate the resonance multiplication in the metal adducts. Quantitative results are given in Table I; some of these data are based on measurements at 40, 60, and 100 Mc. Close agreement, usually within 1%, was obtained between measurements at the different frequencies. Some data using *sym*-tetrachloroethane as a solvent were obtained, to permit measurements up to 90°.

The multiplication of proton resonances for the adducts follows the same pattern as that exhibited by the monofunctional esters reported previously.[2,3] Multiplication is observed only for the β and γ protons of *sec*-alkyl substituents. There is no indication of resonance doubling for the α protons in these radicals or for the protons of the methylene bridge in any of the adducts. However, for both α and methylene bridge protons there are rather large chemical shifts to lower field for the adducts as compared to the resonance positions for the protons in the diphosphonates themselves. As in the previous studies, these observations suggest that otherwise identical protons in β and γ positions in secondary alkyl radicals are in different magnetic environments. Only a very small dependence of shift on temperature was observed, which suggests that either the difference in magnetic environment is due to rapid rotation with a preferred angle of rotation or that there is a preferred conformation with a rather high barrier against rotation. In either case the "up" conformation[3] would serve to allow the different magnetic environment, with the uranyl group replacing the benzene ring as the source of the internal magnetic anisotropy.

The spectra of the 3-methyl-2-butyl adduct at 60 and 100 Mc. (Figure 4) show three distinct γ-methyl doublets of equal intensity and two β-methyl doublets for which the high-field doublet has approximately twice the intensity of the low-field doublet. The β-methine signals also appear to consist of two multiplets, with the high-field multiplet partly superimposed on the low-field β-methyl doublet. A possible explanation for these data is essentially the same as

TABLE I

CHEMICAL SHIFT OF VARIOUS PROTONS OF ADDUCTS AND ESTERS IN $CDCl_3$ SOLUTION, REFERRED TO TETRAMETHYLSILANE

Uranyl nitrate adducts of	Ester (10 vol %), p.p.m.	Adduct 250 g./l., p.p.m.	Difference, p.p.m.
Tetraethyl methylenediphosphonate			
Methylene bridge	−2.45	−3.18	−0.73
α-Methylene	−4.23	−4.45	−0.22
β-Methyl	−1.36	−1.42	−0.06
Tetra-2-propyl methylenediphosphonate			
Methylene bridge	−2.37	−3.03	−0.66
α-Methine	−4.79	−5.19	−0.40
β-Methyl	−1.35	−1.365	−0.015
		−1.575	−0.225
Diethyl di-2-propyl methylenediphosphonate			
Methylene bridge	−2.405[a]	−3.07[a]	−0.665
α-Methylene	−4.19	−4.53	−0.34
α-Methine	−4.785	−5.20	−0.415
β-Methyl (ethyl)	−1.35	−1.385	−0.035
β-Methyl (propyl)	−1.36	−1.435	−0.075
		−1.57	−0.21
Tetra-2-butyl methylenediphosphonate			
Methylene bridge	−2.39	−3.02	−0.63
α-Methine	−4.58	−5.00	−0.42
β-Methyl	−1.34	−1.35	−0.01
		−1.61	−0.27
γ-Methyl	−0.95	−0.87	+0.12
		−1.045	−0.095
Di-*n*-butyl di-2-butyl methylenediphosphonate			
Methylene bridge	−2.42	−3.10	−0.70
α-Methylene	−4.13	−4.48	−0.35
β-Methyl	−1.34	−1.39	−0.05
		−1.60	−0.26
γ-Methyl	−0.94	−0.89	+0.05
		−1.045	−0.105
Tetra-2-amyl methylenediphosphonate			
Methylene bridge	−2.37	−2.98	−0.61
α-Methine	−4.20	−4.50	−0.30
β-Methyl	−1.34	−1.37	−0.03
		−1.62	−0.28
δ-Methyl	−0.93	−0.77	+0.16
		−1.01	−0.08
Tetra(3-methyl-2-butyl) methylenediphosphonate			
Methylene bridge	−2.38	−2.96	−0.58
α-Methine	−4.45	−4.82	−0.37
β-Methyl	−1.29	−1.29	None
		−1.61	−0.32
γ-Methyl	−0.935	−0.89	+0.045
		−1.01	−0.075
		−1.055	−0.12
Lanthanum nitrate adducts of			
Tetra-2-propyl methylenediphosphonate			
Methylene bridge	−2.37	−2.50	−0.13
α-Methine	−4.79	−4.85	−0.06
β-Methyl	−1.35	−1.35	None
Tetra-2-butyl methylenediphosphonate			
Methylene bridge	−2.39	−2.52	−0.13
α-Methine	−4.58	−4.70	−0.12
β-Methyl	−1.34	−1.34	None
		−1.39	−0.05
γ-Methyl	−0.95	−0.93	+0.02
Thorium nitrate adduct of			
Tetra-2-propyl methylenediphosphonate			
Methylene bridge	−2.37	−2.68	−0.31
α-Methine	−4.79	−4.90	−0.11
β-Methyl	−1.35	−1.39	−0.04

[a] Each component of the bridge triplet is further split into a closely spaced triplet.

that offered in a previous paper in this series[3] to explain the spectrum of bis(3,3-dimethyl-2-butyl) phenylphosphate. There are four possible diastereoisomeric configurations for each half of the diphosphonate. Each configuration might place otherwise similar protons in a different magnetic environment. If the synthesis and/or purification of either the extractant or adduct caused the elimination of an isomer in which there is a shift of the β-methyl proton signal to lower field and the γ-methyl proton signal to higher field, the spectra could be as observed. Each of the three isomers that remains could place the γ-methyl protons in a slightly different magnetic environment, while two of the three groups of β-methyl protons are in the same magnetic environment. This explanation assumes that there are no observable interactions between the halves of the diphosphonate since there are a total of eight diastereoisomers possible, which could result in eight sets of resonances.

From the behavior of the methylenediphosphonates as extractants,[6] it appears that these compounds are chelating extractants for lanthanides and trivalent actinides. Chemical analysis and thermogravimetric analysis of the solid adducts show that the chemical composition is $UO_2(NO_3)_2 \cdot P$ (where P represents a methylenediphosphonate molecule). Molecular weight determinations of some uranyl nitrate adducts in chloroform solution are given in Table II. They indicate that in these solutions the uranyl nitrate adducts are chelates. This conclusion is corroborated by the observation that the optical spectra remain unchanged when the concentration of adduct is varied from 10^{-1} to 10^{-3} *M*. Proton magnetic resonance spectra are also the same for 100 and 250 g./l. solutions.

TABLE II

MOLECULAR WEIGHTS OF VARIOUS ADDUCTS IN $CHCl_3$ SOLUTION[a]

Uranyl nitrate adduct of	Calcd. formula wt.	Measd. mol. wt.
Tetra-2-propyl methylenediphosphonate	734	773
Tetra-*n*-butyl methylenediphosphonate	794	796
Di-*n*-butyl di-2-butyl methylenediphosphonate	794	806
Tetra-*n*-amyl methylenediphosphonate	850	876
Tetra-2-amyl methylenediphosphonate	850	848
Tetra-*n*-hexyl methylenediphosphonate	906	853

[a] Molecular weights were determined at several concentrations and extrapolated to infinite dilution.

The chemical shifts observed for the protons in the adducts with uranyl nitrate can be accounted for by considering the magnetic anisotropy of the uranyl group[7] as the most important factor. The model of the magnetic characteristic of the uranyl group proposed by Eisenstein and Pryce[7] depicts this group as a thin cylinder with a paramagnetic field perpendicular to the axis of the cylinder and a diamagnetic field parallel to this axis. The model for bonding to the

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(6) T. H. Siddall, III, *J. Inorg. Nucl. Chem.*, **25**, 883 (1963).

(7) J. C. Eisenstein and M. H. L. Pryce, *Proc. Roy. Soc.* (London), **A229**, 20 (1955).

uranyl group proposed by Coulson and Lester[8] is that of a linear group with bonding of ligands in the equatorial plane. A chelate structure would require the uranium to be bound between the two phosphoryl oxygens with the uranyl oxygens extending, above and below, and perpendicular to the plane of the chelate ring.

Pople, Schneider, and Bernstein[9] give the equation for the chemical shifts to be expected for protons in the neighborhood of such an anisotropic field

$$\Delta\sigma = \frac{\Delta\chi_{\text{atomic}}(1 - 3\cos^2\gamma)}{3R^3} \quad (1)$$

where $\Delta\chi_{\text{atomic}} = \chi_{\text{atomic}}$ (parallel to axis) $- \chi_{\text{atomic}}$ (perpendicular to axis), R is the distance of the proton from the anisotropic atom (or group in this case), and γ is the angle between a line joining the proton to the center of the anisotropic group and the axis of symmetry of the anisotropic group.

Figure 5 gives the contours of magnetic field around the uranyl group calculated from eq. 1. A value of -2.74×10^{-28} was taken for $\Delta\chi_{\text{atomic}}$. This value is based on $+57 \times 10^{-6}$ for the molar susceptibility of the uranyl group and -55×10^{-6} as $\Delta\chi_{\text{molar}}$ (parallel). Einstein and Pryce estimate a value of -50×10^{-6} but suggest that this may be a slight underestimate.

One immediate qualitative feature derived from Figure 5 and structural considerations is that diamagnetic shifts of resonances are much less likely than paramagnetic shifts. The bridge methylene protons are closely restricted to the equatorial plane of the uranyl group and their resonances must experience a strong paramagnetic shift. If the "up" conformation[3] is assumed, it is difficult for the protons of the alkyl side chains to spend much time in the zone of diamagnetism unless forced there by crowding.

The experimental data fit into this pattern. The bridge protons show a strong paramagnetic shift. In the ethyl and 2-propyl adducts, where there is less crowding, no diamagnetic shifts are observed. Curiously enough, for all adducts with β-methyl groups in 2-alkyl radicals the protons responsible for the upfield part of the β-proton spectrum apparently are located in an average position corresponding to the nodal planes of the magnetic field of the uranyl group.

Another point that is consistent with the "up" conformation and the prediction of chemical shifts is the value of the downfield shift for the other half of the β-methyl protons. The "up" conformation requires that these protons should occupy an average position close to the equatorial plane of the uranyl group at a distance of about 6 Å. The observed chemical shifts do indicate consistency with such a position when compared with Figure 5.

Perhaps the best test of the over-all model is a comparison of calculated and observed chemical shifts for the bridge methylene protons of the adducts. The position of these protons relative to the uranyl group is closely fixed, since they are attached to the rather rigid chelate ring. If γ of eq. 1 is taken to be 80° and $\Delta\chi_{\text{atomic}} = -2.74 \times 10^{-28}$, then $\Delta\sigma = -0.9$ p.p.m. for $R = 4.6$ Å., or $= -1.5$ p.p.m. for $R = 4.0$ Å. From consideration of molecular models, a value of 80° for γ and a value in the range of from 4.0 to 4.6 Å. for R appear reasonable. The experimental values from Table I and for a number of adducts not included in the table are all about -0.6 p.p.m. Perhaps the observed agreement is as much as should be expected in view of the accumulated uncertainties in the model.

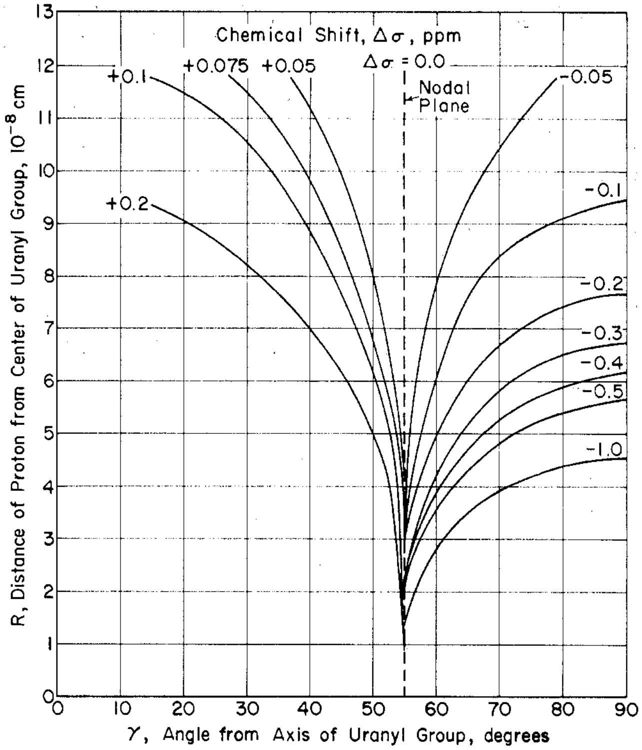

Figure 5.—Magnetic field around the uranyl group.

While we are inclined to believe that the discussion above tends to support, at least in a qualitative manner, the broad combination of (1) the Eisenstein–Pryce magnetic model of the uranyl group, (2) the Coulson model for bonding to the uranyl group, and (3) our own view of the importance of the "up" conformation of organophosphorus esters, we are quite aware that drastic assumptions are involved. The main assumption is that the observed values are due primarily to the anisotropic field of the uranyl group. This can never be more than approximately true. The very process of forming a bond to the uranyl group must alter the electronic shielding of at least those protons that are only a few bonds removed from the phosphoryl oxygen. There is also the possibility that there are effects[10] from the electric field from charge separation within the adduct molecule which, of course, must possess over-all electroneutrality. In the extreme case where the uranyl group is assumed to carry a double charge this could amount to several tenths p.p.m. shift to low field for

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[8] C. A. Coulson and G. R. Lester, *J. Chem. Soc.*, 3650 (1956).

[9] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959.

[10] A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

the bridge protons. However, there seems to be at least some covalent character in the bonds that coordinate the oxygen atoms to the uranyl group and for that reason there is no basis for a quantitative assignment of charge to the uranyl group. There is not any obvious experiment for rigorously separating what might be termed electronic and electric field contributions to $\Delta\sigma$. The closest approach to such an experimental separation of effects is to examine the chemical shifts for adducts that are formed with other metal nitrates. If these metal ions are magnetically isotropic, then the observed shifts must be exclusively due to what we have termed electronic and electric field contributions. The data in Table I for the adducts with lanthanum and thorium nitrates indicate that these contributions may be the lesser fraction of the total. It should be noted that due to the possibility of a large charge on thorium and lanthanum the electric field effect should be even larger than with uranium.

The discussion to this point has also ignored the possible role of the nitrate ions. In the main, this oversight is permissible in a first approximation. The nitrate ion is magnetically anisotropic but $\Delta\chi_{\text{atomic}}$ is only 8×10^{-30}.[11]

Another possible weakness in our explanation is that the uranyl ion may not be strictly linear in all circumstances. While there is considerable evidence for linearity,[12] especially in crystals,[13] there is also some evidence for a bent uranyl ion.[14,15]

(11) K. S. Krishnan, B. C. Guha, and S. Banerjee, *Phil. Trans. Roy. Soc. London*, **A231**, 235 (1933).

(12) L. H. Jones, *Spectrochim. Acta*, **10**, 395 (1958).

(13) W. H. Zachariasen, *Acta Cryst.*, **7**, 795 (1954).

(14) G. K. T. Conn and C. K. Wu, *Trans. Faraday Soc.*, **34**, 1483 (1938).

(15) L. Sacconi, L. G. Caroti, and P. Paoletti, *J. Inorg. Nucl. Chem.*, **8**, 93 (1958).

CONTRIBUTION FROM THE ROCKEFELLER INSTITUTE AND THE
DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK, NEW YORK

The Electronic Structures and Spectral Properties of the Square-Planar Dithiooxalate Complexes of Nickel(II), Palladium(II), Platinum(II), and Gold(III)

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Received December 21, 1964

The electronic spectra of the dithiooxalate (dto^{2-}) complexes of Ni(II), Pd(II), Pt(II), and Au(III) are assigned on the basis of the derived energy levels for the $Ni(dto)_2^{2-}$ complex. These assignments are compared to those proposed earlier for the analogous complexes containing maleonitriledithiolate (mnt^{2-}). The analysis indicates that d → d, charge-transfer, and intra-ligand transitions occur below 50,000 cm.$^{-1}$ in these complexes. The Δ_1 values ($x^2 - y^2 \leftrightarrow xy$ separation) of the dto^{2-} complexes are compared to the Δ_1 values of complexes containing related sulfur-donor ligands.

Introduction

The interpretation of the electronic spectra of planar metal complexes has been a subject of considerable recent interest.[3] For d^8 low-spin complexes containing halide ligands, the charge-transfer bands are of the ligand → metal (L → M) type, while planar complexes containing diatomic ligands with some π-acceptor capability show reasonably low-energy charge-transfer bands of the metal → ligand (M → L) type. For example, $Ni(CN)_4^{2-}$ shows three fairly intense bands between 32,000 and 37,600 cm.$^{-1}$ which are assigned metal(d) → CN(π^*).[4] It is obviously desirable to attempt a classification of the electronic spectra of planar complexes containing ligands which themselves have low-energy absorption bands, indicating a small spacing between the highest filled and the lowest empty levels. In such cases, we may possibly encounter absorption bands due to four different types of transitions: d → d, L → M, M → L, and transitions mainly localized in the ligand system which we shall abbreviate L → L*. Some progress has been made in the interpretation of such complicated spectra, as for example in the planar maleonitriledithiolate complexes[5] and in the four-coordinate β-diketone complexes of Cu(II).[6] In this paper, we shall attempt to interpret the complete electronic spectra of planar $M(dto)_2^{n-}$ (M = Ni(II), Pd(II), Pt(II), and Au(III)) complexes in terms of d → d, L → M, M → L, and L → L* transitions using a molecular orbital theory basis for the detailed assignment scheme.

Experimental

Preparation of Compounds.—Potassium dithiooxalate was obtained from Eastman Kodak and was used as received. The

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(1) Graduate Fellow of the Rockefeller Institute.

(2) Alfred P. Sloan Research Fellow.

(3) Pertinent references are found in the following review: H. B. Gray, *Progr. Transition Metal Chem.*, **1**, in press.

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