Chelate Complexes of Iodonium Cations. Preparation of Dibenziodolium 1,3-Diphenyl-1,3-propanedionate and Dibenziodolium 2,2,6,6-Tetramethyl-3,5-heptanedionate[1]

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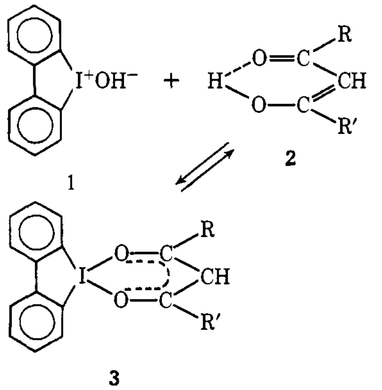
Abstract: Dibenziodolium 1,3-diphenyl-1,3-propanedionate and dibenziodolium 2,2,6,6-tetramethyl-3,5-heptanedionate were prepared by reaction of dibenziodolium hydroxide with the respective β diketones. The neutral 1:1 complexes are yellow crystalline solids, monomeric in benzene solution, nonelectrolytes in *N,N*-dimethylformamide, acetone, and dimethyl sulfoxide, and easily hydrolyzed in aqueous HCl to the β diketone and dibenziodolium chloride. Crystallographic unit-cell data for dibenziodolium 1,3-diphenyl-1,3-propanedionate are reported, as are the uv spectra of both compounds. The ir spectra in the carbonyl region (1500–1800 cm^{-1}) closely resemble those of the normal metal chelates of β diketones and differ from those of the few unusual complexes in which the β diketone is bonded through the central (methylene) carbon atom or through a single oxygen atom. These compounds provide the first reported examples of chelate complexation of a halogen atom.

A great many iodonium salts, $[RIR']^+[X]^-$, have been prepared since Victor Meyer reported the first in 1894.[2] Considerable imagination has been exercised in the synthesis of interesting iodonium cations, mostly substituted diphenyliodonium cations and other diaryliodonium cations together with a few cyclic aryliodonium cations and nonaryliodonium cations.[3] Only rarely, however, have the resulting compounds contained other than simple anions. Sandin isolated diphenyliodonium compounds of several strongly nucleophilic anions and determined the products of decomposition;[4] several interesting betains were described by Neilands a few years ago;[5] and Krause recently prepared diphenyliodonium salts incorporating transition-metal complex anions and described the phenylation of the ligands that occurred during their decomposition.[6]



$R = R' = -C_6H_5$ or $-C(CH_3)_3$

We report here the first chelate complexes of an iodonium cation. Each was prepared by an acid–base reaction between dibenziodolium hydroxide **1** and a β diketone **2**. The products **3** are neutral compounds in which the enolate anion of the β diketone serves as a chelate ligand for the dibenziodolium cation. These compounds provide interesting examples of the tendency, never fully realized, toward metallic behavior in the chemistry of the heaviest of the stable halogens.

Experimental Section

Preparation of Dibenziodolium 1,3-Diphenyl-1,3-propanedionate (dbi-dppd). Dibenziodolium hydroxide (dbi^+OH^-) was prepared by stirring 0.52 g (0.00165 mol) of dibenziodolium chloride (dbi^+Cl^-)[7] with a twofold excess of freshly precipitated and washed Ag_2O in 50 ml of water at 55° for 4 hr. The excess silver oxide was filtered off, and the solution of dbi^+OH^- was stirred at 10° while 0.276 g (0.00123 mol) of 1,3-propanedione (Hdppd, Eastman) dissolved in 15 ml of ethanol was added dropwise. A yellow color was noticed on the first drop, and a lemon-yellow precipitate soon formed. Stirring was continued for 1 hr, after which the yellow precipitate was isolated by filtration, washed with water, and dried *in vacuo*, yield 0.596 g of crude product which softened at *ca.* 70° and melted at 85–90°. This was transferred to the paper thimble of a small Soxhlet extractor and extracted with 17 ml of anhydrous diethyl ether for 1 hr. This ether was discarded, and extraction continued with another 17 ml of ether for 36 hr. The product crystallized in the boiling flask and was isolated by filtration, washed with a little ether, and dried *in vacuo*, yield 0.365 g. The thin yellow platelets melted with decomposition at 110–115°. *Anal.* Calcd for $C_{27}H_{19}IO_2$: C, 64.56; H, 3.81. Found: C, 64.64; H, 3.95.

Preparation of Dibenziodolium 2,2,6,6-Tetramethyl-3,5-heptanedionate (dbi-tmhd). This compound was prepared by the above procedure using 0.12 g (0.00065 mol) of 2,2,6,6-tetramethyl-3,5-heptanedione (Htmhd, Eastman) and 0.32 g (0.0010 mol) of dbi^+Cl^-, yield 0.51 g of crude product melting 106–115° with decomposition. The Soxhlet extraction was carried out using *n*-pentane, and the 0.16 g of pale yellow solid so obtained consisted of microcrystalline needles, mp (dec) 125–128°. *Anal.* Calcd for $C_{23}H_{27}IO_2$: C, 59.75; H, 5.87. Found: C, 59.67; H, 5.91.

Molecular Weight Measurements. Molecular weights in freezing benzene were measured with a standard Beckmann freezing-point apparatus, with care taken to exclude moisture. The measurements were made immediately on freshly prepared solutions because the solutions darken over a period of several hours.

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[1] Financial support for this work was provided by the National Science Foundation under Grant GP-5656.

[2] V. Meyer and C. Hartmann, *Ber.*, 27, 426 (1894).

[3] For a review see D. F. Banks, *Chem. Rev.*, **66**, 243 (1966). See also F. M. Beringer, L. L. Chang, A. N. Fenster, and R. R. Rossi, *Tetrahedron*, **25**, 4339 (1969), and preceding papers.

[4] J. W. Greidanus, W. J. Rebel, and R. B. Sandin, *J. Amer. Chem. Soc.*, **84**, 1504 (1962).

[5] O. Neilands and G. Vanags, *Dokl. Akad. Nauk SSSR*, **129**, 337 (1959) [*Chem. Abstr.*, **54**, 7703*f* (1960)]; O. Neilands, *Zh. Org. Khim.*, 1, 1858 (1965) [*Chem. Abstr.*, **64**, 3396*d* (1966)].

[6] K. K. Ramaswamy and R. A. Krause, *Inorg. Chem.*, **9**, 2649 (1970).

[7] J. Collette, D. McGreer, R. Crawford, F. Chubb, and R. B. Sandin, *J. Amer. Chem. Soc.*, **78**, 3819 (1956).

Mass spectra were obtained with the AEI MS-9 at Harvard University. The source temperature was 230°, well above the melting decomposition temperature of the solid samples. Spectra could not be obtained with the source temperature set at 110°.

Acid Hydrolysis Reactions. Weighed samples of the compounds were stirred in warm 2 *M* HCl for 1 hr. In each case the yellow solids soon disappeared and a white precipitate formed. This precipitate was filtered off, washed with H_2O and then with ether, weighed, and then identified as dbi$^+$Cl$^-$ by its X-ray powder diffraction pattern. The ether washings (above) were combined with an ether extract of the original filtrate. Solid Hdppd was recovered by simple evaporation of the solvent, while Htmhd was isolated as the Cu(II) complex, Cu(tmhd)$_2$, by shaking the ether solution with aqueous cupric acetate.

Electrolytic Conductivity. Conductivities were determined at 25° with a 1-cm Freas cell, calibrated with a KCl solution using an Industrial Instruments RC-16B2 bridge.

Absorption Spectra. The uv spectra were obtained with a Cary 14 spectrophotometer using 1-cm cells, and the ir spectra were obtained with a Perkin-Elmer 337 spectrophotometer using mineral oil and fluorocarbon oil mulls and KBr pellets.

Unit-Cell Determination. The unit cell of dbi-dppd was determined at room temperature using quartz-calibrated (a = 4.913 Å) precession photographs taken with Cu Kα radiation (λ = 1.5418 A). The density was measured by flotation in carbon tetrachloride–hexane. The crystals of dbi-tmpd were too small to permit a preliminary crystallographic examination.

Results and Discussion

Dibenziodolium 1,3-Diphenyl-1,3-propanedionate. Dbi-dppd is a yellow crystalline solid, slightly to moderately soluble in acetone, benzene, ethanol, and dimethyl sulfoxide. The solid can be stored without apparent decomposition for several months, but the solutions darken over a period of several hours at room temperature. The compound reacts rapidly with chloroform, dichloromethane, and 1,2-dichloroethane, precipitating dibenziodolium chloride.

The cryoscopically measured molecular weight of 530 ± 25 in benzene agrees with the value of 502 expected for a monomeric 1:1 complex. The mass spectrum shows a significant peak at m/e = 502, where the parent ion peak is expected. Also present are a number of minor peaks at substantially higher values of m/e, with a significant one at $m/e \simeq 680$. We assume that these result from high molecular weight decomposition products; the source temperature was 230° and the measured decomposition temperature of the solid is 110°. The preliminary crystallographic examination yielded a unit-cell volume and density consistent with a molecular weight of 502.[8]

With the elemental composition and molecular weight established, we sought to determine whether the product could be described as a "complex" between an iodonium cation and the enolate anion of the β diketone or whether a further irreversible reaction had taken place.[9] Simple hydrolysis in aqueous HCl gave dbi$^+$Cl$^-$ in 92% yield and Hdppd in 86% yield, indicating that further reaction had not occurred. The molar electrolytic conductivities of 7.6 ohm^{-1} in dimethyl sulfoxide, 1.7 ohm^{-1} in acetone, and 5.5 ohm^{-1} in *N*,*N*-dimethylformamide demonstrate that dbi-dppd is largely undissociated in these solvents.[10]

Important evidence for a chelate structure is found in the ir spectrum. It seemed possible, although unlikely, that the β diketone might be bound to the iodine through the central carbon atom or through a single oxygen atom. Bonding through the central carbon atom has been observed in trimethylplatinum dipyridyl acetylacetonate and in a number of other platinum complexes.[11] The absorption maxima of highest frequency in the carbonyl region (1500–1800 cm^{-1}) occur below 1650 cm^{-1} in "normal" metal–β diketone chelate complexes and, in the case of the acetylacetonates, have been assigned to a mixture of C=C and C=O vibrations. There are, for example, no significant absorption bands in the 1600–1800-cm^{-1} region in Zn(dppd)$_2$, Cu(dppd)$_2$, or Zn(tmhd)$_2$. However, for platinum acetylacetonates bonded through the central (methylene) carbon, absorption maxima above 1650 cm^{-1} are observed, and the presence of these has been used as a diagnostic test for such bonding.[12] Moreover, it has been suggested on the basis of chemical evidence that mercury(II) complexes of acetylacetone, 2,2,4,4-tetramethylheptanedione, and 3,7-dimethyl-4,6-nonadione are oxygen-bonded simple enolates rather than chelates. These complexes show strong absorption in the 1678–1684-cm^{-1} region.[13]

The ir spectrum of dbi-dppd in the 1500–1800-cm^{-1} region shows bands at 1503 (m), 1510 (sh), 1548 (m), 1585 (m), 1591 (sh), and 1595 cm^{-1} (sh). There is no absorption between 1600 and 1800 cm^{-1}. We consider this to be good evidence that this, like the great majority of metal–β diketone complexes, is a chelate.

The uv spectrum of dbi-dppd (10^{-5} *M* in ethanol solution) shows bands at $\lambda_{\max}$ 343 mμ (ϵ 23,600), 253 (15,300), and 224 (sh on peak at shorter λ). The strong bands at 343 and 253 mμ are found in Hdppd and in metal complexes of its enolate anion. The most notable feature of the spectrum is the absence or substantial shift of the strong band found at 265 mμ (ϵ 20,000) in the spectrum of dbi$^+$ salts of a variety of simple anions, indicating a perturbation of the electronic structure of the dbi$^+$ cation of a kind not characteristic of the simple iodonium salts.

Dibenziodolium 2,2,6,6-Tetramethyl-3,5-heptanedionate. Dbi-tmhd is a yellow crystalline solid quite similar to dbi-dppd. It is somewhat more soluble in petroleum ether, benzene, acetone, and ethanol; but, like dbi-dppd, it reacts rapidly with chlorinated hydrocarbon solvents. The molecular weight in freezing benzene is 451 ± 15, agreeing with the value of 462 expected for the monomer, and the mass spectrum shows a significant parent-ion peak at m/e 462 (there are some lesser peaks at higher values of m/e, including a significant one at m/e 568). The molar conductivity is

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(8) The unit cell is triclinic with a = 16.73 ± 0.06 Å, b = 10.11 ± 0.04 Å, c = 15.07 ± 0.06 Å, α = 116° 8 ± 10 min, β = 108° 25 ± 10 min, γ = 85° 17 ± 10 min, and V = 2166 Å^3. The X-ray density, using Z = 4, is 1.54 ± 0.01 g/cm^3. The measured density is 1.53 ± 0.02 g/cm^3.

(9) Iodonium cations react with nucleophiles at one of the carbon atoms bonded to the iodine. Thus $(C_6H_5)_2I^+Br^-$ decomposes to C_6H_5I and C_6H_5Br. Diphenyliodonium chloride has been used to arylate β diketones at the central carbon atom in liquid ammonia. See Banks, ref 3.

(10) P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956); D. P. Ames and P. G. Sears, *ibid.*, **59**, 16 (1955); M. B. Reynolds and C. A. Krauss, *J. Amer. Chem. Soc.*, 70, 1709 (1948). We measured molar conductivities of 30.3 ohm^{-1} and 27.9 ohm^{-1} for dbi$^+$I$^-$ in dimethyl sulfoxide and *N*,*N*-dimethylformamide, respectively.

(11) A. G. Swallow and M. R. Truter, *Proc. Roy. Soc., Sect. A*, **266**, 527 (1962); **254**, 205 (1960); B. N. Figgis, J. Lewis, R. F. Long, R. Mason, R. S. Nyholm, P. J. Pauling, and G. B. Robertson, *Nature (London)*, **195**, 1278 (1962).

(12) J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, 6740 (1965).

(13) D. C. Nonhebel, *ibid.*, 738 (1963).

4.6 ohm^{-1} in *N*,*N*-dimethylformamide. Acid hydrolysis in aqueous HCl gave dbi$^+$Cl$^-$ in 89% yield and Htmhd (isolated as the Cu(II) complex) in 77% yield. The ir spectrum in the 1500–1800-cm^{-1} region shows absorption bands at 1519 (mw), 1525 (mw), 1558 (m), 1565 (m), 1590 (m), and 1595 cm^{-1} (m). There is no significant absorption between 1600 and 1800 cm^{-1}. The uv spectrum (10^{-5} M in methanol solution) shows a double peak at 266 and 274 mμ (ϵ 19,900) and a shoulder at 224 mμ on an absorption band whose maximum lies at $\lambda < 200$ mμ; it is essentially a superposition of the spectra of the dbi$^+$ ion and Htmpd. The presence of the 265-mμ band (characteristic of the dbi$^+$ cation) in the spectrum of dbi-tmpd, contrasted with its absence in the spectrum of dbi-dppd, suggests that the former is largely dissociated in methanol at 10^{-5} M concentration, whereas the latter suffers very little dissociation in ethanol at the same concentration.

Linear, nonchelate complexes of iodine(I) by nitrogen bases such as pyridine have been recognized for some time.[14] Dbi-dppd and dbi-tmpd are, however, the first reported examples of chelate complexation of a halogen atom. We speculate, on the basis of the simple electron-pair repulsion theory of molecular structure, that the local bonding geometry about the iodine atom is essentially square planar.

We were unable to isolate the corresponding compounds of the diphenyliodonium cation, possibly because the lack of rigid planarity of this cation reduces the activation energy for decomposition by nucleophilic attack by the anion on a carbon atom bonded to the iodine. Perhaps the recently reported and even more rigidly planar 4,5-phenanthryleneiodonium cation[15] will permit the isolation of a greater variety of complexed iodonium compounds.

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(14) J. A. Creighton, I. Haque, and J. L. Wood, *Chem. Commun.*, 229 (1966); S. G. W. Ginn and J. L. Wood, *Trans. Faraday Soc.*, 62, 777 (1966).

(15) See Beringer, *et al.*, ref 3.

Crystal and Molecular Structure of the Macrocyclic Complex, 11,13-Dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II) Perchlorate

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Abstract: The structure of 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II) perchlorate, [NiAT]ClO_4, has been determined by three-dimensional single-crystal X-ray methods. The orthorhombic unit cell dimensions are: $a = 12.385 \pm 0.015$, $b = 14.744 \pm 0.015$, and $c = 8.713 \pm 0.010$ Å, space group *Pbcn*, $d_{\text{obsd}} = 1.56$ g/cm^3, $d_{\text{calcd}} = 1.534$ g/cm^3, $Z = 4$. Intensity data were collected on a Philips PAILRED automated diffractometer with monochromatic Mo Kα radiation. The structure was solved by Patterson and Fourier techniques, and refined by the full-matrix least-squares method to a conventional R factor of 0.072 for the 659 independent nonzero reflections. The [NiAT]$^+$ cation and ClO_4^- anion lie on crystallographic twofold axes. The square planar coordination of the Ni atom has a slight tetrahedral distortion. The Ni–N(trigonal) and Ni–N(tetrahedral) bond distances are 1.83 ± 0.01 and 1.88 ± 0.01 Å, respectively. Bond angles in the 13-membered macrocyclic ligand show that there is some strain associated with the square planar coordination of this relatively small macrocycle. Calculations suggest that square planar coordination of a 12-membered macrocycle is possible; the estimated bonding parameters for such a complex are little different from those of the [NiAT]$^+$ cation. The molecular packing of [NiAT]ClO_4 alternates cations and anions in all three crystallographic directions.

The condensation of triethylenetetraamine (trien) with β-diketones in the presence of nickel(II) yields uninegative tetradentate macrocyclic complexes with 13 atoms in the macrocycle.[1,2] The macrocycles produced, being uninegative with a delocalized ring, are analogs to the corrin ring in vitamin B_{12}.

The structure determination of 11,13-dimethyl-1,-4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II) perchlorate (abbreviated [NiAT]ClO_4; shown schematically below) was undertaken in order to provide information about the bonding of the macrocycle. Square planar coordination about the Ni ion was proposed on the basis of magnetic and spectral data.[1,2] Since most known square planar macrocyclic complexes contain 14 or more atoms in the macrocycle, it was of primary interest to find out how readily the relatively small AT macrocycle accommodates itself to square planar coordination. In particular, it was desired to see if there were signs of strain that would indicate that macrocycles with smaller ring sizes could not hold a metal ion in the macrocyclic plane.

A further goal of the work was to determine the isomeric form in which the complex exists; *i.e.*, there are two possible isomers for square planar coordination of the AT ligand. One has a twofold rotation axis with

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(2) W. H. Elfring, Jr., and N. J. Rose, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 14–18, 1970.