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Hexacoordinated Amine Compounds of Silver (I) and Thallium (I)[a]

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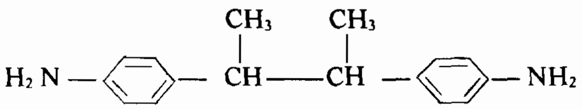
Two complexes of racemic p,p′-diamino-2,3-diphenylbutane (DPB), Tl(DPB)$_3$ClO$_4$ and Ag(DPB)$_3$NO$_3$, are reported. Infrared spectroscopic evidence is used to show that these are hexacoordinated complexes of Tl(I) and Ag(I), with the former being the first reported example of hexacoordinated Tl(I).

Introduction

Marullo and Lloyd have recently reported[1] the formation of water insoluble solid coordination compounds of alkali metal salts with the aromatic diamine, racemic p,p′-diamino-2,3-diphenylbutane, (DPB).



These compounds have the form M(DPB)$_3$X, in which the alkali metal ion is apparently hexacoordinated to the diamine. However, all attempts to form similar compounds with the *meso* isomer of DPB were fruitless, indicating that steric interaction of the methyl groups place the amine nitrogen atoms in a favorable position for complexation with DPB but in an unfavorable position with the *meso* isomer.

These studies have now been extended to include complex compoudns of silver(I) and thallium(I) with DPB. Physical evidence indicates that the compounds reported here are the first example of a hexacoordinated thallium (I) compound, Tl(DPB)$_3$ ClO$_4$, and the first example of a hexacoordinated silver (I) complex, Ag(DPB)$_3$ NO$_3$, in which the donor atom is not a part of a heterocyclic ring.

Silver (I) commonly forms linear complexes having coordination number 2 with ligands, such as N and O, which have little or no dπ bonding capacity.[2] For example, Ag(NH$_3$)$_2^+$ is formed even in solutions of high NH$_3$ concentration and ethylenediamine forms polymeric species with silver (I) and preserves the linear coordination rather than chelating the metal and forming complexes of higher coordination number.[3] With ligands which have some dπ bonding capacity, i.e., with P or S as donor atom, a coordination number of 3 or 4 is not uncommon.[2,4]

Three examples of hexacoordinated silver (I) complexes have been reported. Pfeiffer and Werdelmann[5] reported the first example of 6-coordination for a silver (I) complex in the compound Ag(phen)$_3$ ClO$_4$. However, the structure of this 1,10-phenanthroline compound was not worked out in detail. Prosen and Trueblood[6] reported the dioxane complex Ag(C$_4$H$_8$O$_2$)$_3$ ClO$_4$, with a regular octahedron of dioxane oxygen atoms about each silver and the dioxane acting as a bidentate complexing agent bridging silver atoms in a three dimensional polymeric network. More recently, the pyrazine complex, AgNO$_3$.N$_2$C$_4$H$_4$, was prepared by Schmidt and Trimble[7] and its structure studied by Vranka and Amma[4] by X-ray diffraction techniques. The X-ray analysis revealed that the pyrazine complex is also polymeric with the pyrazine molecule acting as a bridge with each nitrogen on the pyrazine bonding to a different silver atom. The nitrate ions are positioned in the crystal such that four oxygen atoms from the nitrate ions and two nitrogens from different pyrazine molecules form a distorted octahedron, with rather long Ag-O bonds and with the pyrazine nitrogen atoms in the trans position. It is interesting that in each of these complexes the organic molecule is a heterocycle, bonded to the metal atom via a heteroatom.

Very little work has been reported on the coordination chemistry of thallium (I). A coordination number of 4 was found for the thiourea complexes Tl(SCN$_2$H$_4$)$_4$ X,[8] and for the 1-10 phenanthroline complex, Tl(phen)$_2$ ClO$_4$.[5] Perhaps the most unusual compounds of thallium (I) are the thallous alkyloxides reported by Sidgwick,[9] which polymerize to a maximum value of (Tl OR)$_4$. This stoichiometry suggests a cubic arrangement, with Tl and O atoms occupying alternate corners, which gives a coordination number of 3 for the thallium (I).

No examples have been reported previously in which thallium (I) has a coordination number of 6.

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[1] N. P. Marullo and R. A. Lloyd, *J. Am. Chem. Soc.*, *88*, 1076 (1966).

[2] F. A. Cotton and G. Wilkinson, «Advanced Inorganic Chemistry», Second Edition, Interscience Publishers, New York, 1966, pp. 1043-5.

[3] G. Newman and D. B. Powell, *J. Chem. Soc.*, 3447 (1962).

[4] R. G. Vranka and E. L. Amma, *Inorg. Chem.*, *5*, 1020 (1966).

[5] P. Pfeiffer and B. Werdelmann, *Z. anorg. Chem.*, *261*, 197 (1950).

[6] R. Prosen and K. N. Trueblood, *Acta Cryst.*, *9*, 741 (1956).

[7] J. G. Schmidt and R. F. Trimble, *J. Phys. Chem.*, *66*, 1063 (1962).

[8] E. G. Cox, A. J. Shorter, and W. Wardlaw, *J. Chem. Soc.*, 1886 (1938).

[9] N. V. Sidgwick, «The Chemical Elements and Their Compounds», Vol. I, Oxford University Press, London, 1950, pp. 484-5; and N. V. Sidgwick and L. E. Sutton, *J. Chem. Soc.*, 1461 (1930).

Experimental Section

Reagents. Silver nitrate (Baker and Adamson reagent grade) and thallium perchlorate (K & K reagent grade) were dried at 110°C before use. About ten microcuries of thallium-204 in nitric acid (Chem Trac Division of Baird-Atomic, Inc.) was converted to the perchlorate by successive evaporations with perchloric acid. The thallium-204 perchlorate was then taken up in 6 ml deionized water to make a stock solution. Silver-111 was obtained in nitric acid (Isotopes Division, Oak Ridge National Laboratory), and from this solution an aliquot containing about one millicurie of silver-111 was diluted to 100 ml with deionized water to make a stock solution. Dimethylsulfoxide (DMSO) (Matheson, Coleman and Bell spectroquality reagent grade), 95% ethanol (U. S. Industrial Chemicals, Inc., reagent grade) and acetone (Columbia Organic Chemicals Co., Inc., reagent grade) were used as obtained.

dl-p,p′-diamino-2,3-diphenylbutane (DPB). The hydrocarbon, dl-2,3diphenylbutane, was prepared by the method of Barber, Slack and Woolman.[10] The nitration of the dl-hydrocarbon and subsequent reduction to the dl-diamine were performed according to the procedure of Overberger, Marullo and Hiskey.[11] The yield of the dl-diamine based on dl-hydrocarbon was 32.4%. The dl-diamine melted to a colorless, clear liquid at 84-85°C.

Preparation of $Ag(DPB)_3NO_3$. All solvents were saturated with dry nitrogen, and any steps in the preparation that might have allowed air to appreciably contaminate the solvents were conducted under a nitrogen atmosphere, since the diamine in solution is susceptible to oxidation. The samples prepared in the presence of air are usually light tan rather than white.

The diamine and silver nitrate were weighed out in a 3:2 mole ratio, respectively, i.e., 0.1442 g of diamine and 0.1080 g of silver nitrate. The diamine was dissolved in 6.0 ml of 95% ethanol and the silver nitrate was dissolved in 5.5 ml of deionized water. To the aqueous salt solution was added 500 λ of the silver-111 stock solution. A 3.0 ml aliquot was withdrawn from the aqueous, labeled salt solution and added to the diamine solution to give an approximate 3:1 mole ratio of the reactants. The remaining aqueous, labeled salt solution was retained for later use as a standard. Immediately upon mixing the solutions of the reactants, a large amount of fine, white crystalline precipitate was obtained. The precipitate in contact with the mother liquor was refrigerated at 14°C for twelve hours with agitation at frequent intervals. The white precipitate was filtered on sintered glass, washed with a cool 3:1 ethanol-water solution, and dried for 1 hour at 80°C. The yield was 74%. Non-radioactive samples were prepared in the same manner except the silver nitrate was dissolved in 6.0 ml water and no silver-111 solution was added. The compound decomposed at 213-216.5°C to a dark, reddish-brown liquid and a white glass. Tracer studies showed no detectable solubility in water at 30.0°C over an eleven day period, i.e., less than 4.6×10^{-5} mole Ag^+ per liter.

Elemental analysis for silver was performed by withdrawing a 1.00 ml aliquot from the remaining aqueous, labeled silver nitrate solution and counting as the silver standard. A carefully weighed sample of approximately 12 mg of complex was dissolved in 1 ml of DMSO and counted. The counting was done with a well-type 2X2″ NaI(Tl) crystal with a pulse height analyzer, using the 0.34 Mev gamma radiation of the silver-111.

At concentrations of 2×10^{-4} M and below, the silver and thallium complexes were found to be completely dissociated in DMSO to the respective salts and the diamine. A survey ultraviolet absorption spectrum was run on a 1×10^{-4}M diamine solution in DMSO over the range 220-340 mμ and a region of maximum absorption was noted at 304 mμ. Over the concentration range studied the diamine follows the Beer-Lambert law, exhibiting an absorptivity value of 3640 l mole^{-1} cm^{-1} at 304 mμ at a temperature of 22.7°C. A Bausch and Lomb Spectronic 600 with matched 1 cm vycor cells was used for the ultraviolet absorption measurements. By preparing solutions of a known weight of complex which would furnish an amine concentration in the $0.5\text{-}1.0 \times 10^{-4}$M range, the actual weight of amine was determined from the corresponding absorbance values. The slight excess of diamine in the analysis is probably due to an inability to recrystallize the compound. However, the results are reproducible and give a stoichiometry of 1 Ag:3.03 diamine. Anal: Calcd. for $Ag(DPB)_3NO_3$: Ag, 12.1; diamine: 80.9 Found: Ag, 12.4; diamine: 82.9.

Preparation of $Tl(DPB)_3ClO_4$. The precautions involving the exclusion of air again were taken. The diamine and thallium perchlorate were weighed out in a 3:2 mole ratio, i.e., 0.07210 g of diamine and 0.06076 g of thallium perchlorate. The diamine was then dissolved in 6.0 ml of 95% ethanol and the thallium perchlorate was dissolved in 5.75 ml of deionized water. To the aqueous salt solution was added 250 λ of the thallium-204 stock solution. A 3.00 ml aliquot was then withdrawn from the aqueous, labeled salt solution and added to the diamine solution. The remaining aqueous, labeled salt solution was retained as a standard. Upon combination of the diamine and salt solutions, a moderate precipitation frequently formed which was disregarded and which redissolved when the mixture was heated to boiling and evaporated to 6-7 ml. The solution was then cooled to room temperature with an associated formation of white, coarse crystals. The precipitate in contact with the mother liquor was refrigerated for 12 hours at 14°C, filtered on glass, and recrystallized from 3:1 ethanol-water solution. The filtrate was evaporated to approximately 3 ml, cooled to room temperature, seeded with previously recrystallized product, and treated as described above. The total recrystallized product amounted to an 80% yield. The compound melted to a clear, yellowish-tan liquid at 204.5-206°C. Non-radioactive samples were prepared in the same way except the thallium perchlorate was dissolved in 6.0 ml water and no thallium-204 solution

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(10) H. J. Barber, R. Slack and A. M. Woolman, *J. Chem Soc.*, 99 (1943).

(11) C. G. Overberger, N. P. Marullo and R. G. Hiskey, *J. Am. Chem. Soc.*, 83, 1374 (1961).

was added. The solubility was found by tracer studies to be 3.09×10^{-4} mole of Tl$^+$ per liter of water at 30.0°C.

Elemental analysis for thallium was performed by counting the beta radiation of thallium-204, using an end-window Geiger-Muller tube with a 1.6 mg/cm^2 window. A 25 λ aliquot was transferred from the remaining aqueous, labeled thallium perchlorate solution to a 3 ml. cupped planchet, dried, and counted as the thallium standard. A carefully weighed sample of approximately 13 mg of labeled complex was dissolved in 1 ml of acetone, from which a 25 λ aliquot was transferred to a planchet, dried and counted. Self-absorption of the beta radiation was found to be very nearly the same in the standard and the complex, so no corrections were necessary.

The amine analysis was performed as described for the silver compound. In addition, a C, H, and N analysis was made as a supplemental test of the spectrophotometric technique.

Anal: Calcd. for Tl(DPB)$_3$ ClO$_4$: Tl, 19.9; diamine, 70.4; C, 56.2; H, 5.90; N, 8.20.

Found: Tl, 19.7; diamine, 70.9; C, 56.8; H, 6.10; N, 8.20.

Infrared Spectroscopic Data. The infrared spectra for all samples were determined as Nujol mulls sandwiched between sodium chloride discs. Infrared survey spectra were taken on the Perkin-Elmer 137 Spectrophotometer (Fig. 1). The regions of particular quantitative interest were examined using the Perkin-Elmer 221 Spectrophotometer (Fig. 2).

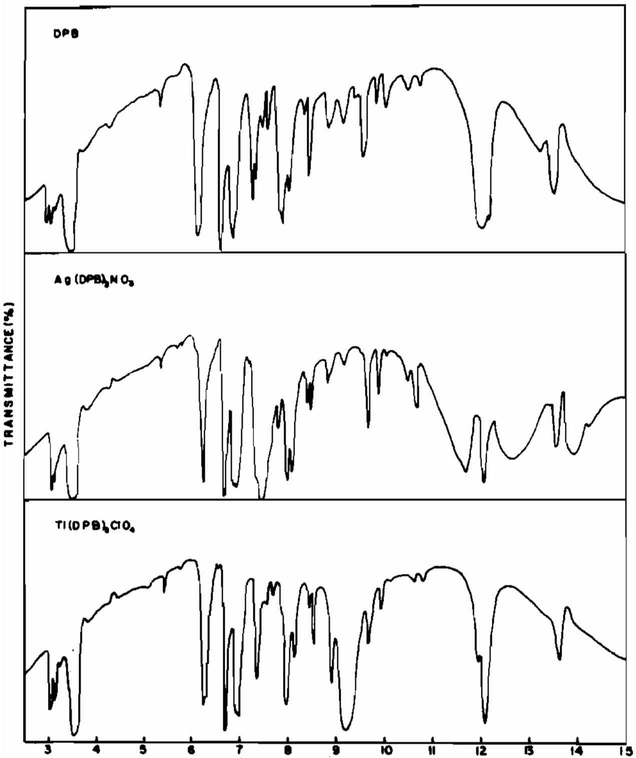

Figure 1. Infrared Spectra of Indicated Compounds.

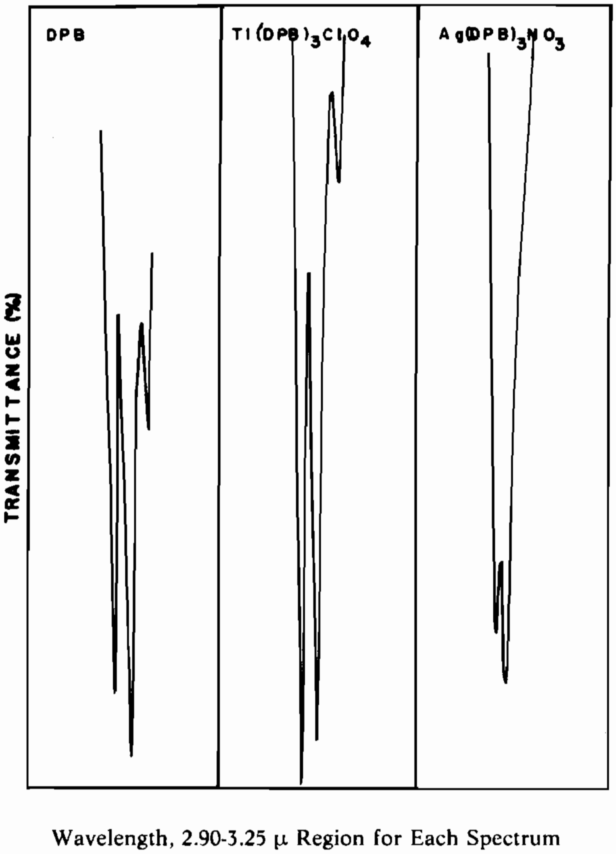

Figure 2. Infrared Spectra of Indicated Compounds, 2.90-3.25 μ Region.

The spectrum of the diamine shows the characteristic bands for the asymmetric and symmetric N-H stretching modes for para-substituted anilines[12,13] at 3389 cm^{-1} and 3292 cm^{-1}, respectively. In the spectrum of Ag(DPB)$_3$ NO$_3$ these bands are moved to lower frequencies, appearing respectively at 3316 cm^{-1} and 3258 cm^{-1}, i.e., shifts of 73 cm^{-1} and 34 cm^{-1}. In the spectrum of Tl(DPB)$_3$ ClO$_4$, the first band is moved to 3371 cm^{-1} and the second remains at 3292 cm^{-1}, i.e. shifts of 18 cm^{-1} and zero. With the exception of the unique lack of shift for the second band in the thallium compound, there was no evidence of any non-bonded amine groups still present in these complexes. The 1389-1333 cm^{-1} and 1034-970 cm^{-1} absorption regions for the silver complex indicated that nitrate was present as the ion, not as a coordinated nitrate group. An intense band occurred at 1347 cm^{-1} characteristic of an ionic nitrate,[14] while no intense band appeared in the 1034-970 cm^{-1} region where the O-NO$_2$ stretching of a coordinated nitrate group has been reported[15,16] to absorb. In the spectrum of the thallium complex an intense band at 1094 cm^{-1} is found, in good agreement with known values for non-coordinated perchlorate

(12) J. Chatt, L .A. Duncanson and L. M. Venanzi, *J. Chem. Soc.*, 2712 (1956).

(13) A. V. Ablov, H. H. Proskina, L. F. Chapurina and V. G. Semina, *Russ. J. Inorg. Chem.*, *10*, 1214 (1965).

(14) J. R. Ferraro, *J. Mol. Spectroscopy*, *4*, 99 (1960).

(15) B. M. Gatehouse, S. E. Livingston and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957).

(16) B. M. Gatehouse, S. E. Livingston and R. S. Nyholm, *ibid.*, 3965 (1958).

ions,[17] and none of the bands reported[18] for coordinated perchlorate were found.

From these data it is reasonable to consider that the metal ions are indeed hexacoordinated solely to the amine groups and that the anions are situated in the interstices of the crystal. Further work on the elucidation of these structures is now in progress. Of principle interest in these studies is to discern whether the ligand is acting as a chelate or if the complexes are polymeric, with the ligand acting as a bridge and to determine the unique structural features of DPB which lead to the formation of these complexes. The result of these investigations will be presented at a later time.

(17) A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, 9, 211 (1959).
(18) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).