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5. SILVER

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CONTENTS

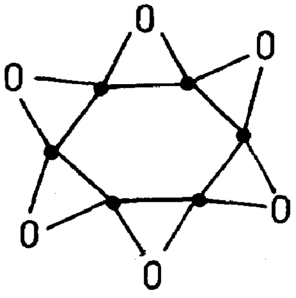
INTRODUCTION

The silver chemistry reported tends to confirm the basic principles worked out over the years with the increasing use of X-ray analysis providing greater definition. It is notable that the coordination numbers and geometry varies with simple ligands and that it is where more complex ligands, macrocycles and clusters are involved that a greater degree of symmetry is imposed on the silver ion.

5.1 COMPOUNDS AND COMPLEXES WITH SIMPLE LIGANDS

Some improvements in our knowledge of relatively simple silver compounds have been reported this year. A second form of Ag_2O was reported some time ago, but it has now been shown to be Ag_6O_2, (*1*), and to consist of a hexagonal arrangement of silver atoms with shared oxygen atoms bridging each silver-silver bond [1].

Complexes of the type $M_2[AgI_3]$ contain $[AgI_3]^{2-}$ units in a pyramidal C_{3v} arrangement in solution, but although an analogous structure is seen in the solid state, (M = K or $[NH_4]$), larger cations force a change in the solid state coordination not observed in solution [2]. Since small bare silver clusters are of importance in latent image photography, the structures of $[Ag_3]$, $[Ag_3]^-$ and $[Ag_3]^+$ have been investigated by theoretical methods [3]. It is suggested



(1; ● = Ag)

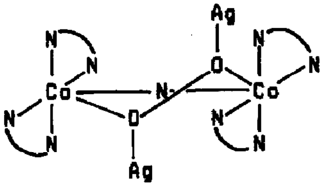
that $[Ag_3]$ and $[Ag_3]^+$ would be triangular and $[Ag_3]^-$ linear. In another study, well-defined UV-visible absorption and fluorescence spectra of $[Ag_2]$ trapped in a rare gas matrix have been reported [4]. Among the new compounds reported is an Ag_3P_{11} species [5], found at the silver-rich end of the silver-phosphorus phase diagram; the silver is tetrahedrally coordinated to the phosphorus. Two new borates, $AgBO_2$ [6] and Ag_3BO_3 [7], were prepared by heating Ag_2O and B_2O_3 in the presence of oxygen under pressure. Heating As_2O_5, $AgNO_3$ and either hydrated cobalt sulphate or zinc sulphate produced compounds of formula $AgM_3H_2(AsO_4)_3$ (M = Co or Zn) [8]. The silver geometry in both compounds is planar and four-coordinate but, in $MAg(NO_3)_2$ (M = K, $[NH_4]$ or Rb), it is a distorted tetrahedral arrangement [9].

A wide range of solvents has been used this year to obtain novel silver species in solution and as isolated compounds. Silver cyanide dissolved in liquid ammonia produces a range of coordination isomers including species such as AgCN, AgNC, $[Ag(CN)_2]^-$, $[Ag(NC)_2]^-$ and $[Ag(CN)(NC)]^-$ [10]. Using a range of solvents, Ag(SCN), $[Ag(SCN)_2]^-$ and $[Ag_2(SCN)_3]^-$ have been prepared in solution [11] with, for example, the first two being detected in thf, the second in dmf and the third in hexamethylphosphoramide. Liquid BrF_3 was used to prepare $AgBF_4$ [12] and in liquid HF, $Ag[UF_6]$ and $Ag[UOF_5]$ can be prepared [13] by mixing solutions of $[UF_6]^-$ and $[UOF_5]^-$ with AgF. These latter two compounds complement the known compounds $Ag[UF_6]$ and $Ag_3[UF_8]$ obtained by heating UF_5 and AgF.

$[Ag(PO_4)]^{2-}$ and $[Ag_2(PO_4)]^-$ have been identified in a potentiometric study in molten nitrate, indicating that the silver-oxygen affinity in phosphates is quite strong [14] and, in an aqueous solution containing perchlorate, Ag(CO) has been identified for the first time. Previously only $[Ag(CO)_2]^-$ had been identified, with Ag(CO) being characterised only in liquid HF [15].

Among the crystal structures of silver compounds reported this year, one solves the problem of the structure of the complex first isolated by Werner in

1910 [16]. It is a silver derivative of a binuclear amido-μ-peroxodicobalt species $[(en)_2Co(NH_2)(O_2)Co(en)_2][NO_3]_3.15/8\ Ag[NO_3].H_2O$ [17]. The silver is in fact directly coordinated to the peroxo bridge, as shown in (2). In the

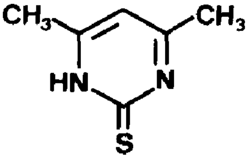


(2)

binuclear complex $[Cu(NH_3)_4][Ag(SCN)_3]$, the silver ions are bridged through the sulphur of the thiocyanate [18], and in $[Co(NH_3)_5(NCSAg)][ClO_4]_3$, the evidence from infrared and Raman spectroscopy is that the silver is again coordinated to the sulphur [19]. In this latter case, the compound is a model for the intermediates present in the catalytic aquation of halide and pseudo-halide complexes of transition metals. The relative 'hardness' of cobalt compared to silver is illustrated by an extension to the chemistry of one of those binuclear compounds. The monomeric complex $[(Ph_3P)_2Co\{AgSCN.SeCN\}_2]$, on dissolution in a range of coordinating solvents such as thf, produces chain compound coordinated through bridging $[SeCN]^-$ and $[SCN]^-$ groups, with the nitrogen atoms coordinated to the cobalt [20].

$[(Ph_3P)_3AgCl]$ contains approximately tetrahedral silver ions with three phosphines and one chlorine attached [21], and in $[(Ph_2MeP)_3Ag(BH_4)]$ it is also tetrahedrally coordinated with a monodentate $[BH_4]^-$ unit completing the coordinate shell [22]. Examples of oxygen coordination for which the crystal structure has been reported include silver(I) malonate, which contains both monocoordinated Ag-O species and five-coordinate silver with four oxygen and one silver ion in the coordination sphere [23]. 4-aminobenzoate complexes with centrosymmetric dimeric units linked by carboxylates and linear chains linked by carboxylate and amine groups have also been reported [24]. 1,2-ethane disulphonate complexes also coordinate through both sulphonate groups, to give sheets of silver ions with long Ag-Ag distances linked by the ligand, but with the more flexible butane ligand, this arrangement breaks down to give a very distorted trigonal bipyramidal arrangement round the silver [25]. Substituted benzene selenato ligands are also bonded to silver through two oxygen atoms [26] and bis(creatinine)silver(I) complexes provide an example of nitrogen coordination [27]. The silver is bonded to two imino nitrogen atoms with the proton transferred to an exo-cyclic nitrogen to produce the charge necessary for the perchlorate salt. However, in (pyridine)(aniline)silver(I) nitrate, a triangular coordination to two nitrogen atoms and the nitrate ion is found [28]. Thus, these structures indicate no real trend in silver coordination, except that it is clear that relatively small electronic or steric effects can produce a large change in geometry.

It is perhaps not surprising, therefore, that crystal structures of silver complexes with more complex ligands produce coordination geometries in which the requirements of the ligand rather than the metal predominate. An example of how subtle the changes can be occurs with (tetraazacyclotetradecane)silver(I), which crystallises out in both a needle form and a block form. In both cases, the silver is coordinated in a planar arrangement to four nitrogens but, in the block form, there is an association with a perchlorate oxygen in an axial position [29]. Other examples of more complex ligands are shown in (*3*)-(*6*).



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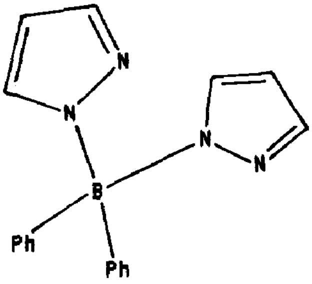

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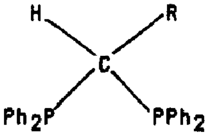

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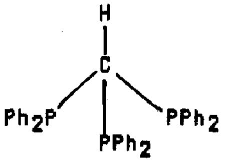


(*6*)

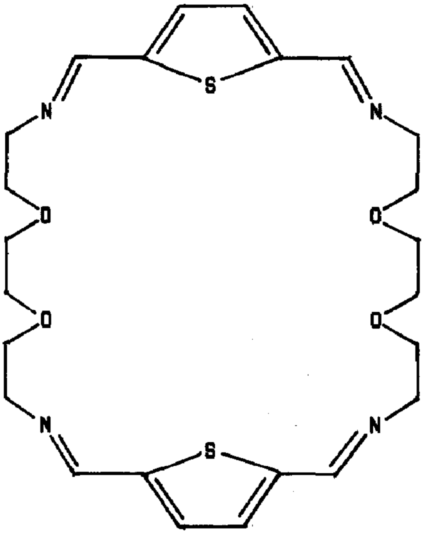
With (*3*), Ag(HL)$_n$X (n = 1 or 2; X = Cl, Bu, I *etc.*) contain *N*- and *S*-bonded ligands but in AgL, the ligand behaves as a tridentate bridging ligand [30]. Ligand (*4*) gives monomeric complexes with the silver trigonally bonded to two nitrogen groups and a phosphine [31], whereas ligands (*5*) and (*6*) form binuclear complexes such as $[L_3Ag_2][BF_4]$ and trinuclear complexes $L_4Ag_3(O_2CR)_3$ [32]; silver-phosphine ring systems are involved in the structures of the complexes with (*5*) and (*6*).

Complexes described this year, in addition to those for which the crystal structure has been elucidated, include examples of sulphur, nitrogen and oxygen coordination. Substituted dithiazole complexes of form AgLX, $AgL_{2.5}X$ and $AgL_{0.5}X$ are coordinated through the ring sulphur and nitrogen mixed ligand [33].

Complexes of pyridine and bipyridine with silver sulphonate contain both nitrogen and oxygen silver bonds [34] and substituted edta complexes contain only silver-oxygen bonds [35]. Other series of complexes with substituted thiobenzoylureas [36], chloro derivatives of diazo amino benzene [37], tetramethylurea [38] and thiodicarboxylic acids [39] have also been reported, and the use of a substituted cystenato silver(I) compound to complex copper(II) has been described [40].

5.2 COMPLEXES WITH MACROCYCLIC LIGANDS

Silver complexes of two new macrocycles have been characterised this year.



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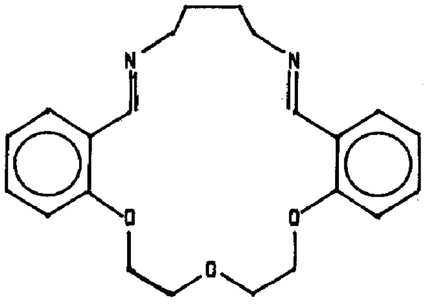
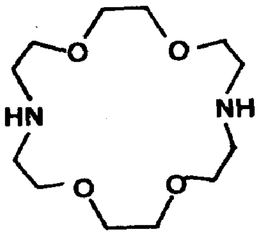


(8)

The X-ray structural analysis of the complex ion $[LAg_2(H_2O)]^{2+}$ {L = (*7*)} shows that the silver is coordinated to nitrogen and oxygen rather than to sulphur atoms [41]. (*8*) produced the complex $LAg(NO_3)(H_2O)$ which, on the basis of infrared evidence, is coordinated to the nitrogen atoms [42]. A range of cryptates of which (*9*) and (*10*) are representative examples produce complexes of formula ML and M_2L [43].

Macrocyclic polythioethers investigated as solvent-extraction agents with picrates gave a range of complexes, including Ag(L)(pic) and $Ag_3(L)(pic)_3$ [44]. The use of crown ethers and picrates for silver extraction was also investigated [45] and a synergistic effect of trioctylphosphine oxide on these systems was



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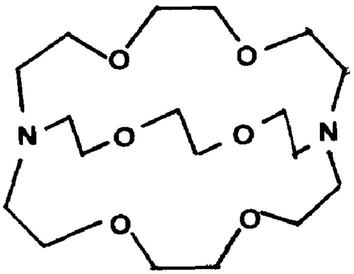

(10)

reported [46].

The stable oxidation states of silver in porphyrins are silver(II) and silver(III), with the silver(I) porphyrin tending to dissociate. This reduction procedure has been followed for substituted porphyrins using pulse radiolysis and, in addition, the free ligand produced could be further reduced and would then react with the silver(II) porphyrin to cause further reduction [47]. The reduction of the silver(II) complex electrochemically is also easier than expected as a result of the tendency of the silver(I) complex to dissociate [48]. The ease of oxidation of these complexes was probed by studying the effect of substituents on the porphyrin ring on silver(II)/silver(III) oxidation. Electron-donating substituents make oxidation easier, electron-withdrawing substituents have the reverse effect [49]. Silver porphyrins give good EPR signals and, rather unusually, spin-spin splitting has been observed [50]. Combined studies of electrochemistry and EPR may therefore shed more light on bonding in these silver complexes. It is a little unusual, in that some other macrocycles accept silver(I) and form stable complexes.

5.3 SILVER CLUSTERS

The increased symmetry and order of silver coordination in macrocycles (Section 5.2) is as expected since it, like the previous simpler systems (Section 5.1), is dominated by ligand effects. However, the inorganic clusters found this year are more unusual, in that they form regular geometries analogous to organometallic systems but for less obvious reasons. Penicillamine forms a well-known series of cluster compounds of general formula

$[\mathrm{M_8}^{\mathrm{I}}\mathrm{M_6}^{\mathrm{II}}\mathrm{L_{12}Cl}]$ $\{\mathrm{M}^{\mathrm{I}} = \mathrm{Cu(I)}$ or $\mathrm{Ag(I)}$; $\mathrm{M}^{\mathrm{II}} = \mathrm{Cu(II)}$, $\mathrm{Mn(II)}$ or $\mathrm{Pd(II)}\}$. This year the crystal structure of the complex with M(I) = Ag(I) and M(II) = Ni(II) was reported [51]. Its structure is analogous to the {copper(I)/copper(II)} case, and consists of a cube of silver ions surrounding a central chloride ion. In addition, each silver is coordinated to three sulphurs in a plane and the nickel ions are arranged around this in an octahedral manner. The complex $[\mathrm{Ag_8(S_2C{=}C(CN)_2)_6}]^{4-}$ has a related structure [52], in that it consists of a cube of Ag(I) ions inscribed in an icosahedron of sulphur atoms in such a way that each silver is again coordinated to three sulphur atoms. However, there is no Cl^- in the centre of the cube, and the silver-silver distance along the edge is shorter. These two compounds raise the question of how widespread inorganic clusters of this type are, and also provide a contrast with the previous part of this report, in that the structures are so regular.

5.4 ORGANOMETALLIC CHEMISTRY

Silver complexes with bonds to rhodium and osmium are reported this year. $\mathrm{Ag[CpRh(CO)(PPh_3)][PF_6].PhMe}$ contains a Rh-Ag-Rh moiety with a bond angle of 171°, and this complex is also a useful source of the reactive radical cation $[\mathrm{RR(CO)(PPh_3)(cp)}]^{+\cdot}$ [53]. $[\overline{\mathrm{Os\{Ag(OClO_3)\}(C}}\mathrm{C_6H_4\text{-}4\text{-}Me)Cl(CO)(PPh_3)_2}]$ contains both a silver-osmium bond and a silver-carbon bond [54]. Other complexes of inorganic interest include a thioether which contains silver bonded both to a sulphur and an alkene [55], a new alkynylide of silver of formula $[\mathrm{M_2\{R(C{=}C)(C_6H_4)\}}]_x$, for which the colour (and probably the structure) depend on the method of preparation [56] and some new silver derivatives of ferrocene [57].

5.5 APPLICATION OF SILVER COMPOUNDS TO ORGANIC CHEMISTRY

Silver compounds are extensively used in organic chemistry and this year is no exception, with examples of oxidative dihydrogenation of alkenes [58], oxidative C-C bond cleavage [59], transfer of alkyl groups from organosilver compounds [60], cycloadditions [61], ring rearrangements [62] and ring openings [63]. In many cases, an organosilver intermediate has been isolated or postulated; for example, in a study of halide extraction from a ferrocene derivative [64]. However, although there are often compounds or complexes of silver isolated during the reactions, it is the organic chemistry which is investigated in detail, and so the field was not reviewed further.

5.6 PHYSICAL METHODS APPLIED TO SILVER COMPOUNDS

Last year the use of ^{109}Ag NMR spectroscopy was reported but, in general, the signal-to-noise ratio is not sufficiently good to make this a useful probe in the chemistry of silver complexes. However, in 1979, Morris and Freeman described a polarisation transfer sequence which enhanced the NMR signals from metals of low gyromagnetic ratio [65]. Called the INEPT sequence (Insensitive Nuclei Enhanced by Polarization Transfer), it involves the transfer of nuclear spin polarisation from nuclei such as protons (which have a large Boltzman population difference) to the nuclear spin of the species under investigation. An example of its use for a silver complex is illustrated in Figure 1 [66]. The improvement in signal-to-noise ratio over conventional ^{109}Ag NMR spectroscopy is clearly illustrated and since long-range metal-proton scalar couplings can be expected in complexes, it should prove a useful addition to the spectroscopic techniques used in silver chemistry.

In other experiments using NMR spectroscopy, ^{13}C NMR shifts from complexed pyridine could be correlated with metal ion charge, but changes in ligand complement were not observable [67]. Proton NMR spectra of silver(I) complexed to l-methionine, l-ethionine and *S*-methyl-l-cysteine indicate amine complexation when the amine is deprotonated [68].

The EPR spectrum of silver(0) in frozen toluene is known, but this year an investigation of frozen solutions of silver(I) perchlorate in aqueous ethanol mixtures after γ-irradiation to produce silver(0) provided spectra both of presolvated silver atoms at 4 K, and solvated atoms at 77 K. There were changes in coordination depending on ethanol concentration and, rather surprisingly at 4 K, the spectra indicated that samples with less than 13% ethanol had a water environment round the silver and above 13% an ethanol one [69]. Using EPR spectroscopy, it was possible to confirm the presence of silver(0) at the centre of a crown ether after γ-irradiation [70].

Some vibrational studies have already been incorporated in previous sections. Other infrared studies include spectra of nitrates at high pressure in which different crystal modifications silver nitrate were detected [71], and a report of a change in structure of the ligand tetrabutyl-S-dithiopyrophosphate on coordination to silver; the P-O-P vibration is lost and new P-S-P and P=O vibrations appear [72]. The resonance Raman effect proved diagnostic of complexation of silver to flavins [73], and the Raman depolarisation ratio was used to detect a phase change in α-AgI at 430 °C [74].

Two more unusual studies appeared this year. Inelastic electron tunnelling spectroscopy [75] was used to study silver clusters supported on

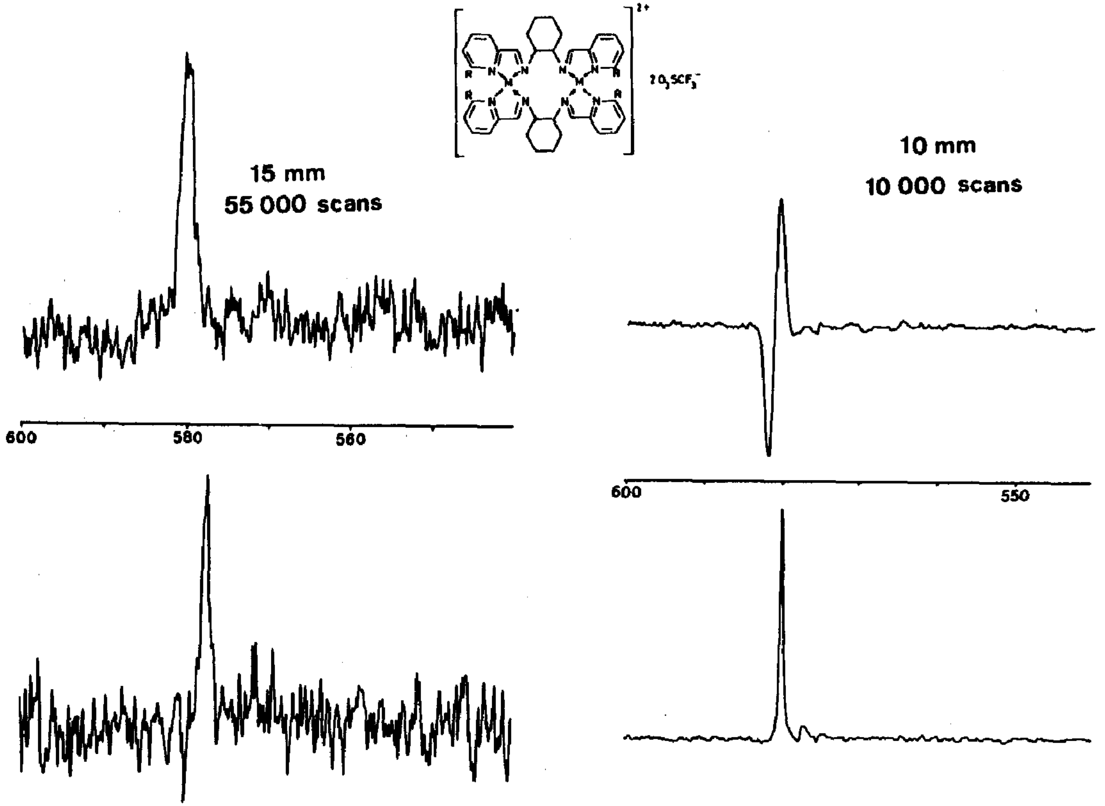

Fig. 1: ^{109}Ag NMR spectra of inset complex (R = H) in CD_3OD. Left; direct observation in a 15 mm probe. Right; INEPT sequence in a 10 mm probe of the same solution. Upper; ^{1}H coupled. Lower; ^{1}H decoupled [66].

aluminium oxide, and He(I) photoemission spectroscopy demonstrated that halide absorption was a function of cluster size for silver, but not for copper [76].

In more traditional inorganic experiments, the stability constants of ten α-amino and silver complexes were measured. In many cases, additional functional groups on the amino and side chains were involved in complexing, but only histidine, methionine and arginine would complex when the amine group was protonated [77].

5.7 CATALYTIC OXIDATIONS

A range of experiments in which silver was used in oxidation or catalytic decomposition reactions has appeared. Hydrogen peroxide oxidation is catalysed by $[Ag(bipy)_2]^{2+}$ ions but it is the $[Ag(bipy)]^{2+}$ ion which is the active species [78]. Peroxymonosulphate decomposition is catalysed by silver peroxydisulphate ion and cobalt ions, and the slow step in the reaction is the reaction of silver with thiosulphate [79]. Fluoroxysulphate oxidation is catalysed by silver(I) [80], and silver(I) and peroxydisulphate catalyse the oxidation of thiourea [81] and of α-valine [82] by a first-order process in $[S_2O_8]^{2-}$. In a study of the role of copper(II) and silver(I) in peroxodisulphate oxidations, only silver acts by direct reaction with oxidant [83].

5.8 SURFACE-ENHANCED RAMAN SPECTROSCOPY (SERS)

Last year a very much increased interest in surface-enhanced Raman spectroscopy (SERS) was reported, and this has continued at such a pace as to preclude systematic coverage each year. The three main areas of interest seem to be in the nature of the effect, in its extension using modifications of the basic technique, and in the application of SERS to new systems. There is, as yet, no evidence of a consensus upon the nature of the effect, although a number of good reviews and papers characterise it and make the options clearer [84-88]. In addition to further papers using electrodes, thin films or sols, SERS from microlithographic silver particle surfaces [89] and a new method of observing molecules on electrode surfaces by potential modulation Raman spectroscopy [90] have been reported. The systems studied this year include chloride-metal bonds formed during the preparation of the electrode [91], various dyes, soluble sulphonated copper phthalocyanine [92], pyridine [93,94], ethanoate [95], cyanide [96,97], $[Ru(CN)_6]^{4-}$ [98], nucleic acid components [99], thiocyanate [100], diphenylthiocarbazone [101], edta [102] and others. The experimentation is not yet quite routine and there are currently no general guidelines to indicate which molecules will give good SERS enhancement but, with continued effort in the field, the work this year shows promise that solutions, both theoretical and practical, will be found in the next few years.

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