GENERAL DISCUSSION

Prof. N. N. Greenwood (*Newcastle upon Tyne*) said: I would ask Perkins to what extent is *d* orbital participation considered to be essential in stabilizing dimeric Al_2Me_6 on this model, and can the absence of such participation in BMe_3 be taken as an important factor in determining its inability to form a stable dimer?

Dr. I. H. Hillier (*University of Manchester*) said: Could Perkins comment on the reliability of the CNDO method applied to the molecules considered in his paper, and on the 3*d* orbital exponent which should be used in such calculations?

Prof. P. G. Perkins (*University of Strathclyde*) said: In reply to Greenwood, we have not yet analyzed the corresponding results for organoboron compounds but believe that the lack of participation of the 3*d* orbitals may well be the factor which militates against formation of compounds such as B_2Me_6.

In reply to Mrs. Green, one should indeed include further bases such as the 4*s* and 4*p* atomic orbitals. However, the whole calculation is subject to a variational procedure and it is the extent to which a set of new functions is likely to contribute which determines their choice.

In reply to Hillier and Urch, the extent to which the *d* orbitals are included is determined by the orbital exponent Z^* and this should be determined during the calculation by minimizing the energy with respect to it. However, such a procedure will be very difficult in the CNDO framework and the present work therefore, as a first approximation, takes two fixed cases. Each compound should be treated on its merits.

In reply to Hill, the orbital exponent Z^* which emerges from a variational calculation need not have any precise physical meaning because it may relate to non-integral numbers of electrons. This is true for simple systems (e.g., He atom) and so Z^* is best regarded as simply a variable parameter defining the 3*d* radial function.

In reply to Hillier, in order to try and assess the reliability of the CNDO method we have made some comparison between it and an extended basis set *ab initio* calculation on $BH_2 \cdot NH_2$. We find that the charge distribution is well reproduced by the CNDO method, and the eigenvalues are in satisfactory agreement. We believe at present that the latter method should be reasonably reliable for differential calculations where gross structural changes are involved.

Prof. Theodore L. Brown (*University of Illinois, Urbana*) said: L. M. Ludwick in our laboratories has recently observed that the presumed 5-coordinate methylcobalt bis-dimethylglyoxime is in fact a dimer in methylene chloride. Dimerization probably occurs through the interaction of an oxygen from one molecule with the axial position of the cobalt atom in a second species. Association in this manner is not uncommon.

We have also been examining the kinetics of exchange reactions involving replacement of the axial ligand in the methylcobalt bisdimethylglyoxime system. Our evidence is not as yet extensive, but there is a suggestion in our results that the ability of the axial ligand to act as a pi acceptor towards cobalt may be an important factor in coordination at this position. For example, triethylphosphite, when bound in this axial position, does not exchange with excess ligand in methylene chloride, as evidence in the n.m.r. spectrum, at temperatures as high as +60°C.

By contrast, nitrogen and oxygen donors typically exchange much more rapidly, with coalescence temperatures of −20 to −50°C.

Dr. H. A. O. Hill (*Oxford University*) said: The suggestion made in the paper by Duncan *et al.* that the field metal *d*-orbitals interact directly with the 1*s*-orbitals of the methyl hydrogens may be most important. What effect would an increasing electron density on a neighbouring metal atom acting directly on the methyl hydrogens have on the J_{H-H} coupling constants?

Prof. Theodore L. Brown (*University of Illinois, Urbana*) said: We have recently observed the ^{35}Cl quadrupole resonance spectrum of Zeise's salt. Absorptions were observed, at 25°C, at 15·9, 20·10 and 20·37 MHz. The latter two absorptions are ascribed to the cis chlorines, which are crystallographically distinct. The lower frequency absorption is assigned to the trans chlorine.

The difference in quadrupole resonance frequencies of the two types of chlorine is substantial, and suggests that ethylene does indeed exert a trans influence insofar as this particular spectroscopic property is concerned. Chlorine quadrupole resonance frequencies can generally be discussed satisfactorily in terms of *p* orbital populations. The quadrupole resonance frequency is a measure of the difference in populations of the p_σ orbital and the p_π orbitals. In the present case, assuming that the asymmetry parameter is small, the lower frequency for the trans chlorine can be explained in terms of a more ionic Pt—Cl bond to the trans chlorine, as a result of a strong σ polarization by ethylene. There may, however, be an additional factor which would decrease the population difference in the p_σ and p_π orbitals, namely, a π-donor action on the part of the trans chlorine toward platinum, resulting from the π-acceptor behaviour of ethylene. I suspect that this is a small effect, and that most of the frequency difference must be ascribed to polarization in the σ bond system. The results are consistent with the observation of Denning regarding the Pt—Cl stretching frequencies in Zeise's salt.

Dr. M. G. Clark (*University of Cambridge*) said: An approach of the type used by Green, Smith, and Tasker may be employed to study the stability of a 4-coordinated square-planar system against the addition of two-electron donating ligands in either or both of the axial positions. The increase in coordination number is assumed to occur without change in spin-state or equatorial bond length.

Consider the effect of adding one or two axial ligands for each realistic ordering of the valence orbitals in a square-planar complex. We may work with the point group C_{4v} appropriate to the addition of one ligand, since the group D_{4h} for the addition of two is related to C_{4v} by the addition of a centre of symmetry. The addition of either one or two ligands may be treated simultaneously, since in the latter case only the centro-symmetric axial-ligand symmetry-orbital has correct symmetry to interact with the orbitals of interest in the complex. The general features of the appropriate energy level diagrams are sketched in fig. 1, using C_{4v} notation. The diagrams may be considered as fragments of more complicated molecular-orbital diagrams, but since we require only qualitative features of the energy levels they are adequate for our purpose, provided that it is borne in mind that they do not show all the interactions between levels explicitly. The only assumption made is that in the enlarged complex the antibonding a_1 orbital is more antibonding than the bonding a_1 orbital is bonding.

For a complex of a metal ion having configuration d^n there are $n+2$ electrons to be assigned to the levels shown in the appropriate diagram. Table 1 shows for

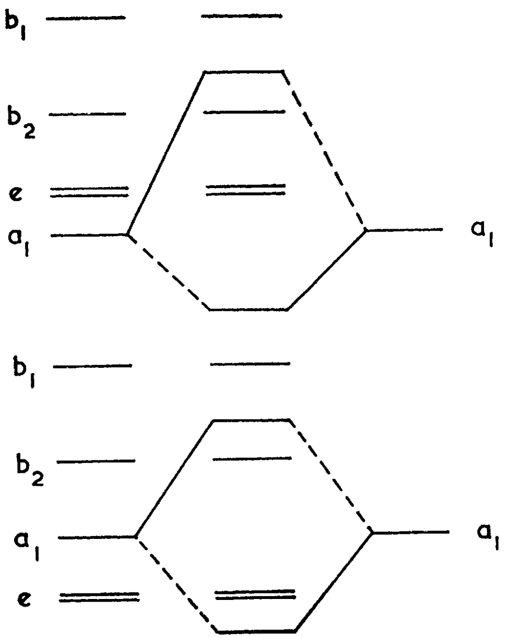

FIG. 1.

TABLE 1

ion	$a_1<e$	$e<a_1$
low-spin d^6	*	*
high-spin d^6	*	u
low-spin d^7	*	*
high-spin d^7	*	u
low-spin d^8	s	s
high-spin d^8	*	*
d^9	s	s

s = stable against addition of ligands ; u = unstable against addition of ligands ; * = may or may not be unstable depending on precise energetics.

$6 \leqslant n \leqslant 9$ the results of considering whether or not the initially square-planar system profits energetically by taking on extra ligands under our assumptions. Not surprisingly, the results are indecisive in several cases ; but two definite points do emerge : (1) d^9 and low-spin d^8 ions are the obvious candidates for forming stable 4-coordinated square-planar complexes, in agreement with observation ; (2) any truly 4-coordinated square-planar complexes of high-spin d^6 and d^7 ions should have $a_1<e$. The rarity of suitable examples makes the second prediction difficult to test ; certainly the mineral gillespite ($BaFeSi_4O_{10}$), in which high-spin Fe^{2+} is square-planar co-ordinated by four oxygens, has $a_1<e$.[1]

The results obtained above should be treated with considerable caution, since, apart from the simplicity of the arguments used, it is not obvious that other factors

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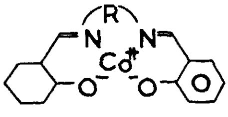
[1] R. G. Burns, M. G. Clark and A. J. Stone, *Inorg. Chem.*, 1966, **5**, 1268 ; M. G. Clark and R. G. Burns, *J. Chem. Soc. A*, 1967, 1034 ; M. G. Clark, G. M. Bancroft and A. J. Stone, *J. Chem. Phys.*, 1967, **47**, 4250.

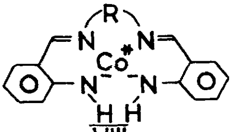
are negligible. For example, the iron in gillespite may have its coordination geometry to some extent forced upon it by the layer structure of the silicate framework.

Dr. H. A. O. Hill (*Oxford University*) said: The apparent reluctance of cobalt amben derivatives to give rise to alkyl cobalt(III) derivatives may be caused by reasons other than those mentioned in the paper by Greene *et al.* Except for ligand (V), only in the amben complexes will the nature of the coordinated nitrogen interfere with the planarity of ligand when complexed. The steric requirements of the NH hydrogens may cause a distortion of the complex such that in the cobalt(II) derivative the structure is intermediate between square-planar and tetrahedral. Even if formed, an alkyl cobalt(III) derivative may be *kinetically* unstable. Though n-propylcobalamin is stable with respect to decomposition in solution, iso-propylcobalamin decomposes by homolytic fission of the cobalt-alkyl bond. This instability is presumably caused by steric interactions of the isopropyl ligand with the ring. Therefore it is possible that the alkyl cobalt amben complexes are unstable, or difficult to isolate, because of steric interaction of the alyl ligand with the non-planar amben ligand.

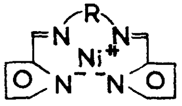
Dr. Michael Green (*University of York*) said: In reply to Hill's remark about the planarity of cobalt amben, conjugated " N_4-type " ligands are remarkable for their tendency to form planar complexes even when geometric factors dictate otherwise. Weber [1] has found that complexes of IX are planar not only when R is —$(CH_2)_2$— and —$(CH_2)_3$— but also when it is —$(CH_2)_4$— in which case a tetrahedral configuration would be preferred sterically. We have found no significant variation either in the visible/ultra-violet spectra or in the magnetic properties of the cobalt amben family (VIII), when R is —$(CH_2)_2$—, —$(CH_2)_3$ or —$(CH_2)_4$—. If a modification in geometry occurred, the first complex would be expected to be planar and the last tetrahedral. (The corresponding compounds from the cobalt salen family (VII) show differences in spectroscopic and magnetic properties [2] compatible with such a modification). Moreover, there is no notable difference between cobalt amben (VIII, R = —CH_2CH_2—), cobalt ambphen (VIII, R = 1,2-phenylene) and the cobalt compound,[3] (X). It is difficult to see how these last two compounds could be distorted tetrahedrally.



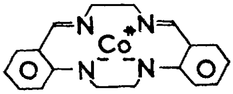
VII



VIII



IX



X

In view of this strong tendency for " N_4 " systems to be planar and in view of their greater field strength compared with " N_2O_2 " ligands, any distortion in an alkylated amben compound would be small and be most likely to involve the cobalt atom moving slightly out of the plane of the ligand which would remain flat as for CH_3CoBAE which Hill mentions.

Dr. H. A. O. Hill (*Oxford University*) said: We have measured the e.p.r. spectra of the mono- and/or dipyridine complexes of the cobalt(II) derivatives of ligands

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[1] J. H. Weber, *Inorg. Chem.*, 1967, **6**, 258.
[2] M. Hariharan and F. L. Urbach, *Inorg. Chem.*, 1969, **8**, 556 and references therein.
[3] M. Green and P. A. Tasker, *Chem. Comm.*, 1968, 518.

I,[1] II,[2] III,[1] IV,[3] VI,[2] and VIII,[2] in the paper by Greene *et al.* and in every case the spectra are interpretable in terms of a low-spin d^7 complex in which the unpaired electron is well-described by the d_{z^2} orbital corresponding to position C and D in fig. 1. It would be of interest to examine the e.p.r. spectra of cobalt(II) amben derivatives.

Dr. Michael Green (*University of York*) (*communicated*): Hill's data for (VII) are interesting as they imply a reversal in the order of the d_{z^2} and d_{xy} orbitals in going from nickel salen to the cobalt salen/pyridine system. The presence of an axial ligand will tend to cause changes A→B→C→D, as we mention in our paper. As cobalt amben is reluctant to add pyridine as a ligand it will have a greater chance of being of A-type than cobalt salen in pyridine. I agree the e.p.r. spectrum will be interesting.

Dr. H. A. O. Hill (*Oxford University*) said: A recent determination of the structure of CH_3CoBAE, which has just been communicated to us prior to publication by Prof. Rondaccio, University of Trieste, Italy,[4] shows that the cobalt is indeed *five-coordinate*, with the BAE ligand planar and the cobalt lying 0·16 Å above the plane of the BAE ligand. Thus, the suggestion made in our paper that in the five-coordinte alkyl Co(III) complexes, the cobalt atom lies above the plane of the ligands is confirmed in this case at least. Such a distribution may have important consequences for the enzymatic role of the five-coordinate complexes. The importance may lie, not in the vacant coordination site trans- to the alkyl ligand but rather, that in the five-coordinate complex, the cobalt and its coordinated alkyl ligand lie out of the plane of the corrin ligand, making both the cobalt and the attached carbon atom more accessible for reaction with the substrate.

Dr. J. F. Ogilvie and **Dr. M. J. Newlands** (*Memorial University of Newfoundland, Canada*) said: One of the most important applications of the theory of bonding in metallo-organic compounds must be to elucidate the binding to metals of reactants, molecular intermediates and products in reactions which are catalyzed by materials containing metals, especially transition metals. A process of some current interest is the fixation of nitrogen in nature, in which molybdenum, perhaps cobalt, and particularly iron are believed to be involved.[5] Inorganic nitrogen complexes of iron have already been prepared.[6, 7] A commonly postulated intermediate in the ammonia-producing process is di-imide.[5] However, di-imide, HN=NH, has been shown to inhibit fixation of nitrogen by, for instance, *Clostridium pasteurianum*.

In connection with our consideration of multiple bonding in silicon and germanium imine derivatives [8] we have been led to suggest that an imine intermediate, M=NH HN=M, rather than M . . . HN=NH . . . M, containing nitrogen atoms strongly bound to the appropriate metal atom M held rigidly in some location by some co-ordinating molecule such as a porphin type of chelating agent. An arylimino complex of rhenium has been prepared [9] which has a relatively short [10] strong bond between nitrogen and rhenium atoms, indicating that such a strongly covalent linkage is indeed possible for transition metals.

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[1] Cockle, Hill, Pratt and Williams, *Biochem. Biophys. Acta*, 1969, **177**, 686.

[2] Hill, Morallee and Pellizer, to be published.

[3] Hill, MacFarlane and Williams to be published.

[4] S. Brucker, M. Calligaris, G. Nardin and L. Randaccio, to be published.

[5] R. Murray and D. C. Smith, *Coord. Chem. Rev.*, 1968, **3**, 429.

[6] A. Sacco and M. Aresta, *Chem. Comm.*, 1968, 1223.

[7] G. M. Bancroft, M. J. Mays and B. E. Prater, this discussion.

[8] J. F. Ogilvie and M. J. Newlands, *Trans. Faraday Soc.*, in press.

[9] J. Chatt, J. D., Garforth, N. P. Johnson and G. A. Rowe, *J. Chem. Soc.*, 1964, 1012.

[10] D. Bright and J. A. Ibers, *Inorg. Chem.* 1968, **1**, 1099.

Prof. N. N. Greenwood (*Newcastle upon Tyne*) said: With regard to Bryce Smith's paper, what is the origin of the antiferromagnetism in the d^{10} compounds formulated as Ag*Br and Ag*I? If there are, indeed, small domains of metal-metal clusters would it not be expected that the compounds would be superparamagnetic rather than antiferromagnetic since the volume exchange interaction energy is known to approach thermal energies for particles smaller than ~100 Å and so magnetic ordering cannot occur?

Prof. D. Bryce-Smith (*University of Reading*) said. In reply to Greenwood, I should state first of all that we have used the term " antiferromagnetism " for convenience because it presently seems to provide the closest description of the observed magnetic behaviour; but we accept that the behaviour is not classically antiferromagnetic. Since Ag^I is isoelectronic with Pd^0, we agree that Ag^I clusters might at first sight exhibit paramagnetic properties similar to those of palladium metal. The different behaviour observed might be explained in several ways, one of which is that we could be dealing with sublattices of Ag^0 and Ag^{II}.

Small domains of metal clusters would lead to superparamagnetism only if these were individually ferro- or ferrimagnetic. Antiferromagnetic domains would not result in superparamagnetism. It is not certain whether metamagnetic domains, i.e., domains in which both ferro- and antiferromagnetic interactions occur, would result in a form of superparamagnetism or what the bulk magnetic properties of a substance containing such domains would be. Certainly, the forms of the curves shown in fig. 5 and 6 are inconsistent wih normal superparamagnetic behaviour.

Dr. M. G. Clark (*University of Cambridge*) said: I would ask Bryce-Smith if it is possible that the new complexes may have polymeric or macromolecular structures with the carbon suboxide, bromide, or iodide acting as bridging ligands. This would help to explain their solid-state magnetic properties and lack of crystalline form, but difficulties might be met with their solution properties and the new form of silver "Ag* ".

Prof. D. Bryce-Smith (*University of Reading*) said. In reply to Clark, the great insolubility of the silver complexes is certainly consistent with polymeric structures. The magnetic properties of the suboxide complexes, in so far as a comparison can be made, appear to parallel those of the derived iodides, a fact which suggests that these properties arise from a common structural feature involving the silver atoms rather than the ligands. For this reason, we believe that super exchange does not contribute in a major way to the magnetic properties, although we do not exclude the possibility that C_3O_2 units can chemically link cluster centres.