681. *Studies in Co-ordination Chemistry. Part XIII.* Magnetic Moments and Bond Types of Transition-metal Complexes.*

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The magnetic moments of octahedral complexes of chromium, manganese, iron, cobalt, and nickel with the chelate groups dipyridyl and a ditertiary arsine are compared. Many of these moments are reported for the first time and the following new compounds are described : [Co(Diarsine)$_3$)](ClO$_4$)$_2$, [Co(Diarsine)$_3$)](ClO$_4$)$_3$, [Co(Diarsine)$_2$(OAc)$_2$](ClO$_4$), [Co(Dipy)$_3$](ClO$_4$)$_3$3H$_2$O, and [Cr(Dipy)$_2$Cl$_2$]Cl,2H$_2$O, where Diarsine = *o*-phenylenebisdimethylarsine and Dipy = 2 : 2′-dipyridyl. Also, the co-ordination of tervalent chromium with a tertiary arsine is reported for the first time. The meaning of the terms " ionic " and " covalent " binding as deduced from magnetic data is discussed. In compounds of the type [M^{II}(Dipy)$_3$]X$_2$, the bonds are ionic ($4s4p^34d^2$) when M^{II} = Mn or Co and covalent ($3d^24s4p^3$) when the metal is Fe or Cr. The nature of the bonds in the corresponding nickel compounds is discussed and it is concluded that the paramagnetism indicates ionic rather than covalent bonds. In the dipyridyl complexes of tervalent Fe and Co the bonds are covalent but the magnetic data are not diagnostic when M^{III} = Cr. No ditertiary arsine complexes of bivalent Cr or Mn were isolated but Fe, Co, and Ni, in their bi- and ter-valent states, all form stable octahedral complexes with this chelate group ; in every case the moments indicate $3d^24s4p^3$ covalent bonds. Certain hypotheses to account for the observed data are proposed. In all cases the moments are consistent with Pauling's theory relating bond type and stereochemistry with magnetic moments.

IN a recent series of investigations (Nyholm, *J.,* 1950, 851, 2061, 2071 ; 1951, 38, 2602) the complexes formed by iron, cobalt, nickel, and copper with the ditertiary arsine chelate group, *o*-phenylenebisdimethylarsine, C$_6$H$_4$(AsMe$_2$)$_2$, were described and their magnetic moments reported. The bivalent complexes of iron, cobalt, and nickel with this chelate group may be oxidised, even by air, to the tervalent compounds which contain strong covalent bonds. The tervalent nickel complexes contain one unpaired electron but these compounds, and particularly the diamagnetic complex salt [Ni(Diarsine)$_3$](ClO$_4$)$_2$, earlier led to some difficulties of interpretation on the simple Pauling theory relating magnetic moment, bond type, and stereochemistry. Also, in contrast with the stability of the iron, cobalt, and nickel compounds, chromium and manganese were reluctant to co-ordinate with the ditertiary arsine. It was considered that a comparative study of the magnetic behaviour of all five metals with dipyridyl and the ditertiary arsine might throw some light on these problems and, accordingly, a summary of the data available in the literature was made. Surprisingly, although dipyridyl complexes of all of these metals have been known for some time, the magnetic moments of several of them had not been reported. These

outstanding values have been determined and the results of this and of previous investigations are summarised in Table 1 and 2. In several cases the values reported by previous workers have been checked.

TABLE 1. *Magnetic susceptibilities of various octahedral complexes.*

Compound	$\chi_g \times 10^{-6}$	$\chi_M \times 10^{-6}$	Diamag. corr.	$\chi_M \times 10^{-6}$, corr.	μ (B.M.)	Ref.
Bivalent : dipyridyl						
[Cr(Dipy)$_3$][Br]$_2$,4H$_2$O	5·57	4,190	375	4,565	3·27	7
[Mn(Dipy)$_3$][Br]$_2$	21·6	14,800	355	15,155	5·98	
[Fe(Dipy)$_3$][ClO$_4$]$_2$	−0·27	−225	—	—	0·0	1, 7
[Co(Dipy)$_3$][ClO$_4$]$_2$	13·2	9,660	350	10,010	4·85	7; cf. 2
[Ni(Dipy)$_3$][I]$_2$,6H$_2$O	4·16	3,700	449	4,149	3·10	7; „ 2
[Ni(Dipy)$_3$][ClO$_4$]$_2$	5·23	3,800	350	4,150	3·10	7;
Bivalent : diarsine						
[Fe(Diarsine)$_2$Br$_2$]^0	−0·3	−236	—	—	0·0	3
[Co(Diarsine)$_3$][ClO$_4$]$_2$	0·85	945	648	1,593	1·92	7
[Ni(Diarsine)$_3$][ClO$_4$]$_2$	−0·38	−423	—	—	0·0	4
Tervalent : dipyridyl						
[Cr(Dipy)$_3$][ClO$_4$]$_3$	6·77	5,610	374	5,984	3·76	7
[Cr(Dipy)$_2$Cl$_2$]Cl,2H$_2$O	12·80	6,480	260	6,740	3·98	„
[Fe(Dipy)$_3$][ClO$_4$]$_3$,3H$_2$O ...	2·32	2,030	405	2,435	2·36	5, 7
[Co(Dipy)$_3$][ClO$_4$]$_3$,3H$_2$O ...	−0·35	−308	—	—	0·0	7
Tervalent : diarsine						
[Fe(Diarsine)$_2$Cl$_2$]ClO$_4$	2·33	1,860	461	2,320	2·34	3
[Co(Diarsine)$_3$][ClO$_4$]$_3$	−0·39	−474	—	—	0·0	7
[Co(Diarsine)$_2$Cl$_2$]ClO$_4$	−0·50	−400	—	—	0·0	6
[Ni(Diarsine)$_2$Cl$_2$]Cl	1·42	1,055	452	1,507	1·89	4

References : (1) Berkmann and Zocher, *Z. physikal. Chem.*, 1926, **124**, 318; Sidgwick, " Electronic Theory of Valency," Oxford, 1927, p. 163; cf. Klemm, Jacobi, and Tilk, *Z. anorg. Chem.*, 1931, **201**, 1. (2) Asmussen, " Magnetokemiske Undersgelser Over Uorganiske Kompleksforbindelser," Copenhagen, 1944, p. 212; Cambi and Cagnasso, *Atti R. Accad. Lincei Rend.*, 1934, **19**, 458; cf. Cambi, Cagnasso, and Tremolada, *Gazzetta*, 1934, **64**, 758. (3) Nyholm, *J.*, 1950, 851. (4) *Idem, ibid.*, p. 2061. (5) Simon, Morgenstern, and Albrecht, *Z. anorg. Chem.*, 1937, **230**, 225; A. Simon and Knauer, *Z. Electrochem.*, 1939, **45**, 678; cf. Walden, Hammett, and Gaines, *J. Chem. Phys.*, 1935, **3**, 364; *J. Amer. Chem. Soc.*, 1936, **58**, 1668; see also Michaelis and Granick, *ibid.*, 1943, **65**, 481. (6) Nyholm, *J.*, 1950, 2071. (7) This work.

Table 2. *Experimental and calculated magnetic moments of octahedral transition-metal complexes.*

	Cr	Mn	Fe	Co	Ni	Cr	Mn	Fe	Co	Ni
	Bivalent compounds					Tervalent compounds				
Calculated magnetic moment for ionic or $4s4p^34d^2$ bonds	4·90	5·92	4·90	3·88	2·83	3·88	4·90	5·92	4·90	3·88
Calculated magnetic moment for covalent $3d^24s4p^3$	2·82	1·73	0·00	1·73	0·00 *	3·88	2·83	1·73	0·00	1·73
Experimental moment of dipyridyl complex	3·27	5·98	0·00	4·85	3·10	3·76	†	2·35	0·00	†
Experimental moment of diarsine complex	†	†	0·00	1·92	0·00	3·9	†	2·35	0·00	1·9

* It is assumed that two electrons are promoted from a $3d$ to a $5s$ orbital in which they are paired.
† Not isolated.

Before discussing these data, it is desirable to comment upon the use of magnetic measurements for distinguishing between " covalent " and so-called " ionic " bonds in metal complexes. These two terms are commonly used to distinguish between two extreme types of binding but the limitations of this terminology are fully recognised. By " covalent " binding is implied the use of strong covalent bonds using deep seated orbitals of the metal atom with maximum electron pairing; by " ionic " binding is meant the formation of bonds without any electron pairing at all, *i.e.*, the moment is the same as that of the free ion when Hund's rule of maximum multiplicity of spins is obeyed. In, *e.g.*, the octahedral complexes of tervalent iron, it is found in practice that the moments are either about 2·3 or 5·9 Bohr magnetons, indicating one and five unpaired electrons respectively if the orbital contribution be ignored in the first case. Those complexes containing one unpaired electron are considered to use octahedral $3d^24s4p^3$ bond orbitals, the two $3d$

orbitals being made available for bond formation by electron pairing; potassium ferri-cyanide is an example of this class of compound. In the more strongly paramagnetic complexes containing five unpaired electrons, *e.g.*, potassium ferrioxalate, none of the five $3d$ orbitals is available for bond formation and hence the moment is the same as if the bonds between the Fe(III) ion and the three oxalate groups were purely electrostatic. How-ever, an Fe(III) complex with five unpaired electrons might also make use of $4s4p^34d^2$ orbitals in resonance with these ionic bonds. The physical properties of ferric trisacetyl-acetone, for example, are such that this compound certainly has some type of covalent bonds present; it dissolves in various organic solvents and volatilises when heated. The magnetic moment precludes the use of $3d^24s4p^3$ bond orbitals and it is considered that higher ($4d$) orbitals are brought into play. This proposal has also been made by Professor Jensen (see Report of the Co-ordination Chemistry Conference, *Nature*, 1951, **167**, 434). Huggins (*J. Chem. Phys.*, 1937, **5**, 527) had earlier suggested that $4s4p^34d^2$ bond orbitals might be used in certain transition-metal complexes.

Pauling (*J.*, 1948, 1461) pointed out that the term " ionic " must not be taken too literally and discussed the possibility of using higher-level covalent-bond orbitals; the possibility of four $4s4p^3$ covalent bond orbitals resonating among the six positions was suggested. Many other workers, *e.g.*, Sugden (*J.*, 1943, 328), have commented upon the unfortunate connotations of the term " ionic." A recent theoretical investigation (Craig, Maccoll, Nyholm, Orgel, and Sutton, unpublished; see also Orgel, *Nature*, 1951, **167**, 434) has shown that the use of the higher $4d$ orbitals for σ bond formation by the transition metals is quite feasible from overlap calculations; further, it has been found that the atoms which favour the use of the $4d$ orbitals of a transition metal are the more electronegative ones, as found· in practice for so-called " ionic " bonds. The use of $4s4p^34d^2$ octahedral bond orbitals should result in bonds which are weaker than those derived from the use of the more deep-seated $3d^24s4p^3$ orbitals. The fact that the use of higher covalent bond orbitals in the so-called " ionic " complexes is quite feasible and permits of a more satis-factory description of a bond whose properties are essentially covalent in the usual sense, raises the point whether one could refer to complexes as using " higher " and " lower " covalent bond orbitals rather than as possessing " ionic " and " covalent " bonds respec-tively. The terms " Normalkomplexe " and " Durchdringungskomplexe " are already commonly used to describe these types. This subject will be discussed further by Craig *et al.*

In Tables 1 and 2 the predicted magnetic moments have been calculated on the spin-only formula, $\mu = \sqrt{n(n+2)}$ Bohr magnetons, where n is the number of unpaired electrons per metal atom. For the transition metals it is commonly assumed that the orbital con-tribution is negligibly small, but it can be quite appreciable in some cases, *e.g.*, bivalent cobalt. The size of this orbital contribution, however, is never such as to lead to any ambiguity as to the number of unpaired electrons in the complexes under examination. Given the number of spins, and the co-ordination number of the metal, the orbitals used for bond formation may often be inferred if a suitable theory is accepted. In Pauling's theory the bond orbitals required for a given shape, here d^2ps^3, are made available either by pairing electrons at lower ($3d$) levels or by elevating them to orbitals above those used for bond formation : an example of the former process is the formation of the diamagnetic ferrous compounds starting with a ferrous ion containing four unpaired electrons; the second type of process is postulated to explain the moment of the $[Co(NO_2)_6]^{4-}$ ion which contains only one unpaired electron instead of the three in the cobaltous ion. This unpaired electron is believed to be promoted to an orbital above the $3d^24s4p^3$ orbitals used for bond formation (Pauling, *loc. cit.*, p. 97). Where this promotion occurs it is to be expected that this electron should be in an excited state and capable of being removed by oxidation fairly easily. With the $[Co(NO_2)_6]^{4-}$ ion this is so, but it is probable that this process of promotion is less common than is often supposed; this is referred to later (p. 3574). An alternative approach to the problem of magnetic moment and complex formation has been made by Van Vleck (" The Theory of Magnetic and Electric Susceptibilities," 1935, Oxford, p. 282; *J. Chem. Phys.*, 1935, **3**, 807). According to his argument the atom retains its spin multi-plicity if the co-ordinated groups are not held to the metal atom by strong forces and hence the magnetic moment of the complex ion is the same as that of the free ion; this is assumed

to occur in the $[FeF_6]^{3-}$ ion in which the forces are assumed to be ionic as in the hydrates. With the $[Fe(CN)_6]^{3-}$ ion, on the other hand, the formation of strong covalent bonds is considered to upset the Russell–Saunders coupling, giving rise to a complex ion containing the smallest rather than the greatest number of unpaired spins, as would be expected from Hund's rule of maximum multiplicity. Fortunately, both theories lead to the same result so far as the moment is concerned in the complexes under examination. Most of the literature has been interpreted in terms of Pauling's theory and that approach is adopted here. Reduction of the moment by Van Vleck's mechanism possibly occurs in certain fluorides of the transition metals, *e.g.*, CoF_3; these are reported upon in more detail by Nyholm and Sharpe (Part XII, *J.*, 1952, 2906).

All magnetic susceptibilities were measured at room temperatures and corrected to 20°, Curie's law ($\chi_M \propto 1/T$) being assumed. In view of the magnetic dilution and small temperature difference from 20° this seems quite justifiable.

In calculating moments in Table 1, allowance has been made for atomic diamagnetism of atoms other than the metal atom itself. As mentioned on p. 3572, moments which are 0·2—0·4 B.M. in excess of the calculated figure for spin only do not lead to any ambiguity, but the apparent moments of certain diamagnetic compounds call for comment. Compounds such as $[Fe(Dipy)_3][ClO_4]_2$ have moments of as much as 0·6—0·7 B.M. after the necessary diamagnetic correction to the molar susceptibility has been made. However, since the magnetic moment is proportional to the square root of the corrected molar susceptibility, $\mu = 2\cdot84\sqrt{\chi_{corr.} \times T}$, it can be shown that a moment of 0·6 B.M. arises from a corrected molar susceptibility of only one-tenth of that required for one unpaired electron. Here we have listed all moments which are less than 0·7 B.M. as formally 0·0, since it is practically certain that they arise from factors other than electron spin. The following could account for these small moments : (*a*) experimental errors in the determination ; (*b*) impurity of the compound ; (*c*) uncertainty in the diamagnetic correction for atomic diamagnetism ; (*d*) temperature-independent paramagnetism. The effect probably arises from a combination of all of these but the correction for diamagnetism in particular is very uncertain in many cases.

Discussion of Results.—The preparation of the various compounds is described in the Experimental section. Wherever possible an attempt was made to obtain the compound in which three molecules of the chelate group are attached to the metal atom, but in some cases compounds in which only two molecules of the chelate are attached were isolated. This occurs most frequently with the tervalent metals and may be caused by the tendency to reduce the charge on the complex ion.

Chromium.—Trisdipyridylchromous bromide was described by Barbieri and Tettamanzi (*Atti R. Accad. Lincei*, 1932, **15**, 877) as the black hexahydrate; using a similar method of preparation, we obtained a tetrahydrate on drying. The moment of this compound (3·27 B.M.) indicates $3d^2 4s 4p^3$ bonds. The complex cyanide $K_4Cr(CN)_6$, for which Hume and Stone (*J. Amer. Chem. Soc.*, 1943, **65**, 1200) reported $\mu = 3\cdot15$ B.M., seems to be the only other bivalent chromium complex known in which electron pairing occurs. These authors also report the moments of a large number of chromous complexes containing ionic bonds. With tervalent chromium the compounds $[Cr(Dipy)_3][ClO_4]_3$, first prepared by Barbieri and Tettamanzi (*loc. cit.*), and $[Cr(Dipy)_2Cl_2]Cl,2H_2O$ were isolated, but the magnetic moments (*ca.* 3·9 B.M.) give no information as to the bond type since both ionic and $3d^2 4s 4p^3$ bonds result in the presence of three unpaired electrons. No chromous complexes of the ditertiary arsine were isolated but tervalent chromium forms a readily hydrolysable deep blue complex of the probable formula $[CrCl_2(Diarsine)(H_2O)(C_2H_5 \cdot OH)]Cl$; however, the moment is again *ca.* 3·9 B.M. and is not diagnostic of bond type but is recorded to show that no electron pairing occurs.

Manganese.—The moment of the compound $[Mn(Dipy)_3]Br_2$ indicates five unpaired electrons, showing that no electron pairing occurs. Goldenberg (*Trans. Faraday Soc.*, 1940, **36**, 847) has summarised the magnetic data for a large number of manganese compounds and finds that for Mn(II) electron pairing occurs in the complex cyanide $K_4[Mn(CN)_6],3H_2O$ only; the moment of this compound is 2·18 B.M. All attempts to obtain complex compounds of manganese with the ditertiary arsine have failed.

Iron.—The red trisdipyridylferrous complexes have been reported by several workers to be diamagnetic, with $3d^2 4s 4p^3$ bonds. The related chelate group p-phenanthroline behaves similarly. Tervalent iron forms both a blue trisdipyridyl ion, $[Fe(Dipy)_3]^{3+}$, and a brown binuclear ion $[(Fe(Dipy)_2(OH)_2]^{4+}$, for both of which the magnetic moments (2·1—2·4 B.M.) indicate $3d^2 4s 4p^3$ bonds (see references to Table 1). No compounds of the type $[Fe(Diarsine)_3]X_2$ have been isolated, but those with the formula $[Fe(Diarsine)_2X_2]^0$ are diamagnetic; ferric iron forms the cation $[Fe(Diarsine)_2X_2]^+$ (X = Cl or Br) very readily, and in both ferrous and ferric compounds the moments indicate $3d^2 4s 4p^3$ bonds (see Part III, *J.*, 1950, 851).

Cobalt.—Cobaltous compounds of the type $[Co(Dipy)_3]X_2$ were first described by Blau (*Monatsh.*, 1896, **19**, 647) but the magnetic moment has not been measured previously. The moment of the perchlorate (4·85 B.M.) indicates ionic bonds. For the bromide of the corresponding o-phenanthroline complex, Cambi and Cagnasso (*Atti R. Accad. Lincei*, 1934, **19**, 458) reported the value 5·1 B.M. The tervalent cobalt compound $[Co(Dipy)_3][ClO_4]_3, 3H_2O$, like all octahedral cobalt complexes with the exception of the fluoride, is diamagnetic with $3d^2 4s 4p^3$ bonds. By variation of the technique used in Part V (*J.*, 1950, 2071), the trisdiarsine complex $[Co(Diarsine)_3][ClO_4]_2$ has been isolated, one molecule of the chelate being replaced fairly readily in the presence of suitable substituents. The magnetic moment of this compound (1·92 B.M.) indicates maximum electron pairing and $3d^2 4s 4p^3$ bonds. As mentioned previously, it is necessary to promote this unpaired electron into a higher orbital in order to make the $3d^2 4s 4p^3$ octahedral bond orbital available for bond formation. This electron probably goes into a $5s$ orbital where its removal by oxidation should take place easily. This is in accord with our observation that in aqueous-alcoholic solution the compound $[Co(Diarsine)_3][OAc]_2$ is oxidised rapidly by air to the corresponding cobaltic compound which was isolated as the diamagnetic perchlorate. In the presence of acetic acid in excess, this cobaltic complex loses one molecule of the chelate group to give a red, diamagnetic bisacetato-compound with the formula $(Co(Diarsine)_2(OAc)_2]ClO_4$. The trisdiarsine compound offers a unique opportunity for the resolution of an octahedral cobaltous compound with covalent bonds; preliminary indications that this can be achieved have already been obtained by Dr. D. D. Brown, with whom the resolution of this substance and its oxidation product is being investigated.

Nickel.—The red trisdipyridyl complexes of bivalent nickel have been studied by many workers since they were first prepared by Blau (*loc. cit.*). The resolution of the $[Ni(Dipy)_3]^{++}$ ion by use of active tartaric acid (Morgan and Burstall, *J.*, 1931, 2213) proves that the six bonds are octahedral. The moment has been measured by many investigators (see Table 1), and although values varying between 2·8 and 3·1 B.M. have been reported, the disagreement is unimportant here since the results unambiguously indicate the presence of two unpaired electrons. However, the orbitals which these two orbital electrons occupy have been the subject of much discussion (see Pauling, *loc. cit.*, p. 117; Palmer, "Valency Theory," Cambridge, 1944, p. 178; Eméleus and Anderson, "Modern Aspects of Inorganic Chemistry," Routledge, 1938, p. 176). We take the view that no promotion of electrons occurs in this ion, the two unpaired electrons still being in a $3d$ shell. If this promotion did occur, allowing $3d^2 4s 4p^3$ bonds to be used, then the two unpaired electrons would be promoted either to a $5s$ orbital in which their spins would be paired, or, less likely, remain unpaired by being promoted one to a $5s$ and one to a $5p$ orbital. In the accepted sequence of energy levels, the $5s$ is below the $4d$ and, following the usual procedure in atom building, it is always found that two *paired* electrons are placed in an s orbital before the filling up of p orbitals begins. Thus we expect that, if the bonds were $3d^2 4s 4p^3$, then the ion would be diamagnetic whereas the observed paramagnetism, corresponding with two unpaired electrons, suggests that two unpaired $3d$ electrons are present and hence that the bonds are ionic ($4s 4p^3 4d^2$). The fact that oxidation of the trisdipyridyl nickel complex to a compound of quadrivalent nickel has not been achieved supports this view. Furthermore, the proposal is consistent with the observed diamagnetism of the $[Ni(Diarsine)_3]^{++}$ ion, which is much more stable, suggesting the use of $3d^2 4s 4p^3$ bond orbitals. The use of $4d$ orbitals for σ bond formation is discussed in more detail by Craig *et al.* (*loc. cit.*) where further support for the above view is adduced. The

compound [Ni(Diarsine)$_3$][ClO$_4$]$_2$ was isolated as a deep red powder (Part V, *J.*, 1950, 2061) during the preparation of compounds of the type [NiCl$_2$(Diarsine)$_2$]Cl. The former is not oxidised by air, but in aqueous solution it is oxidised immediately by chlorine, ceric sulphate, or permanganate to give a green solution; addition of perchloric acid to the solution produces a yellowish-green perchlorate which apparently contains tervalent nickel since it is paramagnetic. Unfortunately, the compound could not be obtained pure because on oxidation there is a marked tendency to lose one molecule of tertiary arsine; nevertheless, the fact that [Ni(Diarsine)$_3$][ClO$_4$]$_2$, unlike the dipyridyl complex, can be oxidised supports the view that the bonds are $3d^2 4s 4p^3$. Many tervalent nickel complexes of the type [NiX$_2$(Diarsine)$_2$]Y have been isolated, all having a magnetic moment corresponding with one unpaired electron. Still further oxidation of these compounds yields deep blue complexes of the type [NiCl$_2$(Diarsine)$_2$][ClO$_4$]$_2$, the diamagnetism of which indicates that the nickel atom is now quadrivalent (Part IX, *J.*, 1951, 2602). The isolation of these Ni(IV) complexes provides strong support for the electronic arrangement proposed for the Ni(II) and Ni(III) complexes.

Before attempting to account for the electron pairing it is desirable to summarise some general conclusions from a survey of the experimental results. (1) Whereas dipyridyl may co-ordinate with these transition metals by means of ionic *or* covalent bonds, the ditertiary arsine forms complexes containing covalent bonds only. (2) Manganese and, to a lesser extent, chromium show the greatest reluctance to co-ordinate with the ditertiary arsine; the reluctance of these metals to co-ordinate with the less electronegative ligands has been noted by Sidgwick (" The Chemical Elements and Their Compounds," Oxford, 1950, pp. 1010, 1286). (3) The magnetic moments of all of the compounds can be accounted for satisfactorily on Pauling's theory, by suitably pairing and promoting electrons where necessary; however, it is suggested that promotion occurs less readily than is sometimes assumed, the ligands making use of higher-level, but weaker, bonding orbitals. (4) Wherever both co-ordinate with the same metal the ditertiary arsine is more effective than dipyridyl in causing electron pairing. (5) As expected, both chelate groups co-ordinate more strongly than the corresponding simple, non-chelating ligands, pyridine and dimethylphenylarsine.

Much experimental evidence is available concerning the stability in aqueous solution of complex compounds of the first transition series with a variety of ligands (Burkin, *Quart. Reviews*, 1951, **5**, 1); most of the work concerns the metals in their bivalent states and is therefore relevant to this investigation. Examination of the work of Mellor and Maley (*Nature*, 1947, **159**, 370; 1948, **161**, 436) and of Irving and Williams (*ibid.*, 1948, **162**, 746) reveals that, irrespective of the ligand used (provided that no electron pairing occurs), the order of stability of complexes of the first transition series in aqueous solution is Mn^{II} < Fe^{II} < Co^{II} < Ni^{II} < Cu^{II} > Zn^{II}. Except where steric effects are operative, the same order is preserved with polydentate groups (Schwarzenbach, *Angew. Chem.*, 1950, **62**, 218). Departures from this order have been attributed by Irving (see Report of Co-ordination Chemistry Conference; Wilkins, *Nature*, 1951, **167**, 434) to steric factors or to a change in the bond orbitals used for bond formation.

It is suggested that the major factor responsible for electron pairing and strong binding in certain of these compounds is the formation of strong double bonds (π bonds) using $3d$ electron pairs of the transition metal, as originally proposed by Pauling (*loc. cit.*, p. 250; see also more detailed references in Part X, *loc. cit.*) for complex cyanides, carbonyls, and nitro-complexes. In the case of dipyridyl the $3d$ electron pairs of the metal would need to make use of a p orbital of the nitrogen atom, whilst a vacant d orbital would be used with the arsenic atom of the ditertiary arsine. The single- and double-bond structures contributing to the resonance hybrid in each of the two cases are shown below :
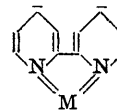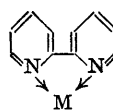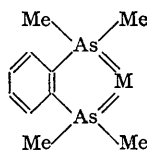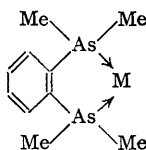
The extent of double bonding will obviously be influenced by the nature of the ligand, the overlap between the d orbital of the metal and the vacant p or d orbital of the nitrogen or arsenic atom, and the number of $3d$ electrons of the metal available for bond formation. As mentioned on p. 3572, the theoretical feasibility of double bonds in these complexes has been established from overlap integral calculations (Orgel, Report of Co-ordination Chemistry Conference, *loc. cit.*). As for the relative ability of the ditertiary arsine and dipyridyl to form double bonds, it is noteworthy that, whereas in the former the use of an already vacant d orbital is involved, in the latter a redistribution of charge is necessary, leaving the carbon atom *para* to the nitrogen with a considerable negative charge. This could occur only to a limited extent, and therefore we might expect to find that double bonding was less with dipyridyl than with the ditertiary arsine. This view is supported by the values of the force constants of the C–O bonds in $Ni(CO)_4$, $Ni(CO)_2$Diarsine, and $Ni(CO)_2$Dipy (Nyholm and Short, unpublished). These are approximately 15.9×10^5, 15.6×10^5, and 14.6×10^5. If we ascribe the gradual weakening of the C–O bond to increasing double-bond character in the Ni–C bond, then the percentage double-bond character decreases in the order Ni–C in $Ni(CO)_4$ is just $>$ Ni–As in $Ni(CO)_2$Diarsine $>$Ni–N in $Ni(CO)_2$Dipy. This is in accord with other experimental observations. So far as data are available, all groups which cause electron pairing with the bivalent transition metals, *e.g.*, CN, NO_2, CO, tertiary arsines, tertiary phosphines, the glyoximes, etc., permit of double-bond structures being written. This does not hold for certain of the tervalent transition metals, *e.g.*, Co(III), which more closely resemble the heavier Group VIII metals as the valency increases, with a tendency to form strong covalent bonds with even the most electronegative atoms; thus, even the hexahydrate $[Co(H_2O)_6]_2(SO_4)_3$ is diamagnetic (Asmussen, *loc. cit.*).

We suggest that electron pairing occurs provided the σ bond is reasonably strong and where the double bonding occurs to an extent sufficient to promote electrons where necessary. Considering first the dipyridyl complexes, double bonding is sufficient to cause electron pairing with Cr(II) and Fe(II) but not with Mn(II), Co(II), and Ni(II). The failure to observe electron pairing with Mn(II) seems to lie partly in the weakness of the σ bond, indicated both by the position of Mn(II) in the Mellor–Maley series and by its low electronegativity, and partly in the peculiar stability of the half-filled $3d$ shell. An arrangement of five unpaired electrons is known from atomic theory to be associated with special stability and hence an even greater reluctance than usual for electron pairing to take place (see Pauling, Victor Henri Memorial Volume, Liége, 1948, p. 8). Another factor is operative in the cases of Co(II) and Ni(II); here the necessary $3d^24s4p^3$ orbitals can be made available only by promotion of electrons above the $4p$ level. To effect this promotion evidently requires the use of groups with greater capacity for double-bond formation than that which occurs with dipyridyl. On the other hand, the ditertiary arsine causes electron pairing with all three metals, Fe(II), Co(II), and Ni(II). This is taken to indicate that the ditertiary arsine forms double bonds much more readily than dipyridyl, thus overcoming the expected weakness of the σ bond arising out of the lower donor capacity of arsenic as compared with nitrogen. Table 3 shows the relative capacities of different groups to effect electron pairing along the sequence iron, cobalt, and nickel. The cyanide group has not been included since this forms four-covalent rather than octahedral complexes with Ni(II). If they can be isolated it is expected that Cr(II) complexes of the diarsine will involve electron pairing and $3d^24s4p^3$ bonds.

With the tervalent elements, dipyridyl complexes of Cr(III), Fe(III), and Co(III) have been isolated and the magnetic moment agrees with $3d^24s4p^3$ binding in all cases; Cr(III) is uncertain, since the magnetic moment is not diagnostic of bond type, but the marked stability of Cr(III) complexes makes it very probable that lower d orbitals are used in the binding. The reason for the failure to isolate Mn(III) and Ni(III) complexes of dipyridyl is uncertain, unless double bonding is insufficient to cause electron pairing, since it would be expected that the Ni(III) complex would be stable only if electron pairing took place.

All ditertiary arsine complexes show maximum electron pairing, and strong covalent $3d^24s4p^3$ bonds are formed in all cases. It is noteworthy that either electron pairing occurs or no complex can be isolated; this suggests that the single σ bonds are weak, at least in

comparison with dipyridyl, and that double bonding is a major factor in their stability. This is not unlikely since it is known that there is some parallel between the proton affinity of a ligand and its ability to co-ordinate with metals which cannot form double bonds, *e.g.*, boron; whereas dipyridyl definitely has some basic tendencies, forming salts with strong acids, the ditertiary arsine will not do this. The reluctance of manganese to co-ordinate is again evident and is attributed to the reasons given above.

Several possibilities for further investigation arise out of this survey. It will be of interest to compare the ability of various substituted dipyridyl derivates to co-ordinate with transition metals on the one hand and with those which cannot form double bonds on the other. Thus, of 4 : 4′-dimethyl- and 4 : 4′-dichloro-2 : 2′-dipyridyl, the former should have the higher basicity and hence the greater co-ordinating ability towards metals which do not form double bonds. However, the chloro-derivative is the one which favours de-localisation of charge from the nitrogen and hence the formation of double bonds.

TABLE 3. *Effect of various groups on type of binding in metal complexes.*

Group and complex	Transition metal and type of binding		
	Fe^{II}	Co^{II}	Ni^{II}
Ethylenediamine [M(en)$_3$]$^{2+}$	Ionic [1]	Ionic [2]	Ionic [3]
Dipyridyl [M(Dipy)$_3$]$^{2+}$	Covalent [4]	Ionic [4]	Ionic [4]
Nitrite group [M(NO$_2$)$_6$]	Covalent [5]	Covalent [5]	Ionic [6]
Diarsine group [M(Diarsine)$_3$]$^{3+}$ or [M(Diarsine)$_2$X$_2$]^0	Covalent [4]	Covalent [4]	Covalent [4]

References : [1] [Fe(en)$_3$]$^{2+}$: $\mu = \sim 5\cdot0$ B.M. (Kanekar and Nyholm, unpublished). [2] [Co(en)$_3$]$^{2+}$: $\mu = 4\cdot9$ B.M. (*idem*; Mellow and Goldacre, *Proc. Roy. Soc. N.S.W.*, 1940, **73**, 233, reported $\mu = 3\cdot8$ B.M.). [3] [Ni(en)$_3$]$^{2+}$: $\mu = 3\cdot0$—$3\cdot2$ B.M. (Cambi, Cagnasso, and Tremolada, *Gazzetta*, 1934, **64**, 758; Cambi and Tremolada, *ibid.*, 1935, **65**, 322; Field and Vosburgh, *J. Amer. Chem. Soc.*, 1949, **71**, 2398). [4] This paper, p. 3575. [5] [Fe(NO$_2$)$_6$]$^{4-}$: $\mu = 0\cdot9$ B.M. (Asmussen, *Z. anorg. Chem.*, 1934, **218**, 425). [6] [Co(NO$_2$)$_6$]$^{4-}$: $\mu = 1\cdot9$ B.M. (Cambi and Ferrari, *Gazzetta*, 1935, **65**, 1162). [Ni(NO$_2$)$_6$]$^{4-}$: $\mu = 3\cdot1$ B.M. (*idem, ibid.*).

EXPERIMENTAL

The following preparations are reported in some detail only when the compounds are new or where modifications have been made to the original method of isolation.

*Tris-*2 : 2′-*dipyridylchromium*(II) *Dibromide Tetrahydrate.*—Freshly prepared chromous acetate (10 g.) was treated with air-free hydrobromic acid (constant-boiling; 30 ml.), previously just decolorised by boiling it with a few drops of hypophosphorous acid, in a stream of carbon dioxide. The flask was cooled in ice, and the blue precipitate of chromous bromide washed twice with small quantities of ice-cold air-free distilled water. Dipyridyl (1·0 g.), dissolved in water (10 ml.) containing 10N-hydrochloric acid (4 drops), was then added to the chromous bromide, followed by a large excess of solid sodium bromide. The black crystalline complex was precipitated instantly, and this was filtered off after cooling at 0° in carbon dioxide for ½ hour. The compound (0·9 g.) was washed twice with ice-cold distilled water and once with alcohol, and then dried in a partly evacuated desiccator over calcium chloride, the tetrahydrate being formed (Found : C, 47·25; H, 4·6; N, 11·0; Br, 21·0; Cr, 6·7. Calc. for C$_{30}$H$_{24}$N$_6$Br$_2$Cr,4H$_2$O : C, 47·7; H, 4·25; N, 11·15; Br, 21·3; Cr, 6·9%). The compound was stored under carbon dioxide. Although stable in dry air, it was oxidised rapidly in aqueous solution, the colour changing from dark brown to yellow.

*Tris-*2 : 2′-*dipyridylchromium*(III) *Perchlorate.*—This salt was made from the foregoing bromide by shaking it with aqueous 5% perchloric acid in air; the yellow deposit was separated and crystallised from warm water (Found : Cr, 6·4; N, 10·1. Calc. for C$_{30}$H$_{24}$O$_{12}$N$_6$Cl$_3$Cr : Cr, 6·35; N, 10·3%).

*Bis-*2 : 2′-*dipyridyldichlorochromium*(III) *Chloride Dihydrate.*—Anhydrous chromic chloride (1·5 g.) and 2 : 2′-dipyridyl (4·7 g.) in alcohol (50 ml.) were mixed and heated to boiling after addition of a trace of zinc dust as catalyst. A vigorous reaction took place, the chromic chloride dissolving to a deep brown solution. The mixture was kept at the b. p. for ten minutes and then allowed to cool; dark red-brown crystals separated and were filtered off and dissolved in a small quantity of hot water. This solution was filtered and allowed to crystallise; the complex *chloride* separated as dark brown crystals which were air-dried (Found : C, 48·1; H, 4·27; N, 10·9; Cr, 10·6; H$_2$O, 7·4. C$_{20}$H$_{16}$N$_4$Cl$_3$Cr,2H$_2$O requires C, 47·5; H, 3·95; N, 11·05; Cr, 10·3; H$_2$O, 7·35%).

*Tris-*2 : 2′-*dipyridylmanganese*(II) *Bromide.*—Manganous sulphate tetrahydrate (2·2 g.)

was dissolved in water (10 ml.) and treated with 2 : 2'-dipyridyl (4·7 g.), and the mixture heated and stirred until the base dissolved. A few drops of alcohol were added to assist solution of the last traces of diamine. The yellow solution was then filtered and cooled, and a solution of potassium bromide (10 g.) in water (50 ml.) added; a yellow microcrystalline precipitate separated. The complex *bromide* was filtered off, recrystallised from hot water, and air-dried (Found : C, 52·7; H, 3·5; N, 12·3; Mn, 7·9. $C_{30}H_{24}N_6Br_2Mn$ requires C, 52·4; H, 3·8; N, 11·4; Mn, 8·0%).

Tris-2 : 2'-dipyridylferrous Perchlorate.—2 : 2'-Dipyridyl (2·0 g.), dissolved in hot distilled water (300 ml.), was treated with excess of ferrous sulphate and sodium perchlorate solution. The red solution was heated on the water-bath for one hour and then left to cool. The red crystalline perchlorate (3·3 g.) which separated was filtered off, well washed with distilled water, and dried *in vacuo* (Found : C, 49·8; H, 3·4; N, 11·5. Calc. for $C_{30}H_{24}O_8N_6Cl_2Fe$: C, 49·7; H, 3·3; N, 11·6%).

Tris-2 : 2'-dipyridylferric Perchlorate Trihydrate.—Ferrous sulphate heptahydrate (1·0 g.) in distilled water (70 ml.) was treated with 36N-sulphuric acid (0·2 ml.) and 2 : 2'-dipyridyl (1·5 g.), and the blood-red solution filtered. The ice-cold solution was saturated with chlorine and warmed to room temperature, a deep blue colour developing. More chlorine was passed in to ensure complete oxidation and excess of 30% sodium perchlorate solution was then added, and the solution allowed to cool in ice. Blue-green crystals of the *perchlorate* were formed; these (1·3 g.) were filtered off, well washed with distilled water, and dried *in vacuo*. In sunlight the compound gradually became red (Found : C, 41·0; H, 4·0; N, 9·2. $C_{30}H_{24}O_{12}N_6Cl_3Fe,3H_2O$ requires C, 41·1; H, 3·4; N, 9·6%).

Tris-2 : 2'-dipyridylcobalt(II) *Perchlorate.*—A solution of cobaltous chloride hexahydrate (0·6 g.) in alcohol (25 ml.) was filtered, boiled to remove air, and treated with dipyridyl (1·2 g.) in hot alcohol (20 ml.), the solution becoming brown. Carbon dioxide was passed into the mixture, which was then diluted with air-free distilled water (50 ml.), and excess of sodium perchlorate was added. After 15 minutes in ice, the salt was filtered off, well washed with distilled water, and dried *in vacuo* (Found : C, 50·2; H, 3·6; N, 10·9. Calc. for $C_{30}H_{24}O_8N_6Cl_2Co$: C, 49·6; H, 3·3; N, 11·5%).

Tris-2 : 2'-dipyridylcobalt(III) *Perchlorate Trihydrate.*—Cobaltous chloride hexahydrate (2·4 g.) and 2 : 2'-dipyridyl (4·7 g.) were heated with distilled water (50 ml.) until complete solution had occurred. The yellow solution was treated with hydrogen peroxide (10 ml.; 30%) and hydrochloric acid (10 ml.; *d* 1·18), and the mixture evaporated to a syrupy consistency. Water (50 ml.) was then added, and the solution treated with perchloric acid (10 ml.; 60%), the yellow crystalline perchlorate then separating. This was recrystallised from hot water and air-dried (Found : C, 41·0; H, 3·4; N, 9·55; Co, 6·6; H$_2$O, loss at 110°, 5·2. Calc. for $C_{30}H_{24}O_{12}N_6Cl_3Co,3H_2O$: C, 41·1; H, 3·5; N, 9·5; Co, 6·7; H$_2$O, 6·1%).

Tris-o-phenylenebisdimethylarsinecobalt(II) *Perchlorate.*—Anhydrous cobaltous acetate (0·3 g.) was dissolved in aqueous alcohol (1 : 1; 20 ml.) containing 17N-acetic acid (2 drops), and the hot solution filtered. After being boiled free from air, the solution was treated with the ditertiary arsine (0·8 g.) dissolved in air-free alcohol, and evaporated *in vacuo* (Found : C, 32·3; H, 4·3%). $C_{30}H_{48}O_8As_6Cl_2Co$ requires C, 32·3; H, 4·3%). The substance is insoluble in water but is moderately soluble in nitrobenzene, nitromethane, and benzonitrile.

Tris-o-phenylenebisdimethylarsinecobalt(III) *Perchlorate.*—Cobaltous acetate (0·2 g.) in distilled water (15 ml.) containing 17N-acetic acid (3 drops) was treated with the ditertiary arsine (0·8 g.) in absolute alcohol (30 ml.). The brown solution was heated to boiling and then freely exposed to the air for 23 hours, during which the brown solution became yellow. Excess of perchloric acid (60%, 5 ml.) was then added, and the solution heated on the water-bath. After a few seconds the microcrystalline yellow *perchlorate* separated; it (0·8 g.) was filtered off, well washed with water and alcohol, and dried *in vacuo* (Found : C, 29·4; H, 3·8. $C_{30}H_{48}O_{12}Cl_3As_6Co$ requires C, 29·6; H, 3·95%). The compound has solubilities similar to those of the corresponding cobaltous complex.

Di-o-phenylenebisdimethylarsinediacetatocobalt(III) *Perchlorate.*—This *salt* was prepared in exactly the same way as the preceding compound, except that a deficiency of the arsine was used and a large excess of acetic acid added. After being left for 24 hours the solution had a reddish-pink colour. Excess of perchloric acid followed by distilled water was added, and a red precipitate was formed. This was recrystallised from hot water containing a trace of acetic acid, glistening red crystals being obtained (Found : C, 34·0; H, 4·6. $C_{24}H_{38}O_8ClAs_4Co$ requires C, 34·0; H, 4·5%).

Tris-2 : 2'-dipyridylnickel(II) *Iodide Hexahydrate.*—Prepared according to Morgan and

Burstall (*J.*, 1931, 2213), the compound was obtained as a pink crystalline powder (Found : C, 40·9; H, 4·1; N, 8·9. Calc. for $C_{30}H_{24}N_6I_2Ni,6H_2O$: C, 40·6; H, 4·1, N, 9·4%).

Tris-2 : 2'-dipyridylnickel(II) *Perchlorate.*—Prepared as for the iodide, this was obtained as a pink crystalline powder (Found : C, 49·4; H, 3·5; N, 11·4; Ni, 8·0. Calc. for $C_{30}H_{24}O_8N_6Cl_2Ni$: C, 49·6; H, 3·3; N, 11·6; Ni, 8·1%).

Reaction of Chromic Chloride with the Ditertiary Arsine.—Chromic chloride tetrahydrate (0·6 g.), dissolved in alcohol (10 ml.), was treated with the ditertiary arsine (1·2 g.) (Cr : di-arsine = 1 : 2), dissolved in alcohol (15 ml.), and the green solution heated to boiling. A blue colour gradually appeared and this deepened when the solution was left for 48 hours. Most of the alcohol was evaporated off on the water-bath, the residue dissolved in chloroform and filtered, and the filtrate treated with light petroleum, a sticky blue precipitate being formed. This was recrystallised twice from a chloroform and light petroleum, the first greenish fraction being rejected on each occasion. A beautiful blue powder was obtained. Analysis indicated that the compound $[CrCl_2(Diarsine)(EtOH)(H_2O)]Cl$ was impure, but in nitrobenzene the molar conductivity (0·8 mho at $c = 3 \times 10^{-3}M$) indicates that the substance is almost a non-electrolyte. The compound is readily soluble in alcohol, acetone, nitrobenzene, chloroform, and nitromethane, but not in benzene or light petroleum, and dissolves in water only with decomposition. It reacts readily with aqueous silver nitrate solution to give a white precipitate. The gram-susceptibility ($\chi_g = 11\cdot3 \times 10^{-6}$) led to $\mu = \sim3\cdot9$ B.M.

Magnetic-susceptibility Measurements.—The Gouy method was employed, the balance described by Baddar, Hilal, and Sugden (*J.*, 1949, 132) being used.

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