THE RELATIVE AFFINITIES OF LIGAND ATOMS FOR ACCEPTOR MOLECULES AND IONS

By Sten Ahrland, J. Chatt, and N. R. Davies

(Akers Research Laboratories, Imperial Chemical Industries Limited, Welwyn)

In 1941 Sidgwick [1] summarised the few available data on the relative affinities of the commoner ligand atoms for various acceptor molecules and ions. Since then the experimental material has increased enormously, and so it seems profitable to attempt a revised and extended correlation involving all the ligand atoms except hydrogen. Admittedly, the quantitative data concerning the heavy donor atoms of Groups V and VI are still sparse, but together with semiquantitative and qualitative evidence there are sufficient to provide a fairly coherent picture. On the other hand, in the case of Group VII where the affinities of the simple halide ions for metal ions can usually be measured conveniently in aqueous solution, the number of quantitative data is now considerable.* [2]

The Relative Co-ordinating Affinities of Ligand Atoms from the Same Group.—There is no uniform pattern of relative co-ordinating affinities of all ligand atoms for all acceptor molecules and ions, not even when only simple unidentate ligands of closely analogous structures are considered, *e.g.*, the alkyl derivatives PR_3, R_2S, etc. Rather, their relative affinities depend on the acceptor concerned. Thus towards trimethyl gallium [3] the relative tendencies of the alkyls of co-ordinating atoms from Groups V and VI to form complexes under comparable conditions are $N > P > As > Sb$ and $O > S < Se > Te$, but towards platinum(II) the order appears to be $N \ll P > As > Sb$ [4] and $O \lll S \ggg Se < Te$,[5] and towards silver $N \lll P > As$ [6] and $O \lll S < Se < Te$.[3, 7] Other similarly diverse examples could be given.

In spite of this lack of uniformity two regular features have emerged: (1) There is in general a very great difference between the co-ordinating affinities of the first and the second element from each of the three Groups of ligand atoms in the Periodic Table, *i.e.*, between N and P, O and S, F and Cl. (2) There are two classes of acceptor: (*a*) those which form their

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[1] Sidgwick, *J.*, 1941, 433.

[2] " Stability Constants ", Part II, by J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, The Chemical Society, London, 1958, pp. 88—127.

[3] Coates, *J.*, 1951, 2003.

[4] Chatt, *ibid.*, p. 652.

[5] Cf. Chatt and Venanzi, *J.*, 1955, 2787.

[6] Ahrland, Chatt, Davies, and Williams, *J.*, 1958, 276.

[7] *Idem*, *ibid.*, p. 264.

* Equilibrium data have been chosen as a measure of stability because they are the only quantitative data widely available. Heats and entropies are still sparse.

most stable complexes with the first ligand atom of each Group, *i.e.*, with N, O, and F, and (*b*) those which form their most stable complexes with the second or a subsequent ligand atom.

In this context each oxidation state and perhaps even each magnetic state must be regarded as a different acceptor ; *e.g.*, copper(I) is markedly different from copper(II) in its complex chemistry, and the different oxidation states of iron also behave very differently towards one and the same donor.

Most metals in their common valency states belong to class (*a*). It also contains the hydrogen ion, and therefore the affinities of ligands for class (*a*) acceptors tend to run roughly parallel to their basicities, except when steric and other factors intervene. The acceptors of class (*b*), which are less numerous, are almost all derived from a number of neighbouring elements occupying an area of more or less triangular shape in the Periodic Table. The base of this triangle stretches, in the sixth period, from about tungsten to polonium and its apex is at copper, copper(I) being a definite class (*b*) acceptor and copper(II) on the border between the classes.

The most pronounced class (*b*) acceptors are formed by elements in the central part of this area. These are the metals which form stable olefin complexes, *viz.*, Cu(I), Rh(I), Pd(II), Ag(I), Pt(II), and Hg(II).[8] Evidently the co-ordination of carbon as a ligand atom, *e.g.*, in ligands such as C_2H_4, CO, and CNR, occurs only to acceptors of a pronounced class (*b*) character. Class (*b*) character appears to depend on the availability of electrons from the lower *d*-orbitals of the metal for dative π-bonding.[9]

The type (*a*) or type (*b*) character of many acceptors is so well defined that they can be classified beyond any doubt even from purely qualitative observations of the stabilities of their complexes, but this is not the case in the border region. On the contrary the boundary is somewhat diffuse, mainly because the various oxidation states of the border elements have different characters. But even when the oxidation state is specified the boundary still remains slightly diffuse, depending in its detail on the specific Group of ligand atoms under consideration. The transition between classes (*a*) and (*b*) within the Periodic Table is thus a more or less gradual one, as visualised in Table 1, where a tentative classification of the acceptor atoms in their normal valency states is given. The border region around the core of pronounced class (*b*) acceptors is fairly extensive. In this region, exact quantitative determinations are necessary to determine the character of a certain acceptor towards a given Group of ligand atoms.

The border is most clearly marked to the right of Group VIII because multiple valency is not common in this part of the Periodic Table and the number of acceptor atoms to be considered is small, also the transition in the character of the acceptors is rapid (compare Ag^+ and Cd^{2+} in Tables 2 and 5). The border almost certainly runs between copper and zinc, and between cadmium and indium. Thallium, lead, bismuth, and tellurium

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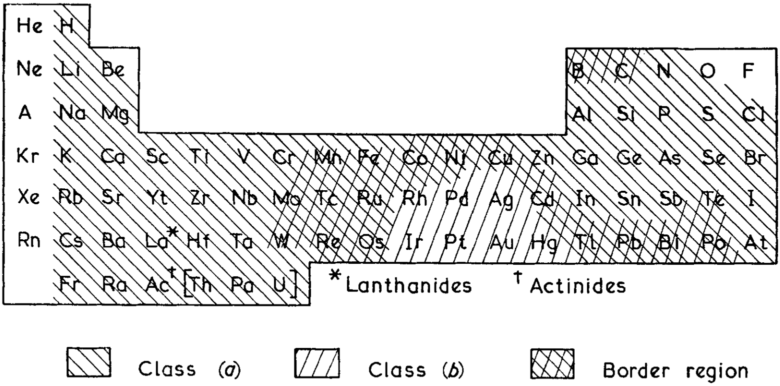
[8] Leden and Chatt, *J.*, 1955, 2936.

[9] Chatt, *Nature*, 1950, **165**, 637 ; Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332 ; Jaffé, *J. Phys. Chem.*, 1954, **58**, 185.

are all border-line elements, and according to their complex halides[10–14] just on the side of class (*b*). Copper(I) is in class (*b*), but cobalt(II), nickel(II), and copper(II) are on the border, having a weak class (*a*) character towards halide ions,[15–17] and a weak class (*b*) character towards Group VI[18] and perhaps Group V ligand atoms.

TABLE 1. *Classification of acceptor atoms in their normal-valent states*



It is surprising that the halide ions follow so closely the pattern of stabilities set by the uncharged atoms of Groups V and VI. Since they are negatively charged, and neutralisation of charge occurs when they form complexes with positive ions, the changes in hydration during the formation of complexes should introduce an important perturbing factor. Nevertheless the pattern of halide-complex stabilities appears to follow in its main features that deduced from complex formation by ligands containing uncharged ligand atoms from Groups V and VI.

To the right of the copper Group of acceptors the higher-valent states have a greater class (*b*) character than the lower-valent states of the same element. This is to be expected because the electrons which enter the metal during its reduction do not enter the *d*-orbitals, which are filled, but the *s*-orbitals where they will screen the *d*-orbitals making them less available for dative π-bonding. Thallium(I) and thallium(III) in their complex halides provide a case in point. The few data, which relate only to halide ions,[10, 11] indicate that both valency states are class (*b*) acceptors and that thallium(III) has by far the stronger class (*b*) character.

[10] Nilsson, *Arkiv Kemi*, 1957, **10**, 363.

[11] Benoit, *Bull. Soc. chim. France*, 1949, 518; Grenthe and Norén, personal communication.

[12] Biggs, Parton, and Robinson, *J. Amer. Chem. Soc.*, 1955, **77**, 5844; Karlsson, personal communication.

[13] Ahrland and Grenthe, *Acta Chem. Scand.*, 1957, **11**, 1111.

[14] Aynsley and Campbell, *J.*, 1957, 832.

[15] Carleson and Irving, *J.*, 1954, 4390.

[16] Ahrland, *Acta Chem. Scand.*, 1956, **10**, 723.

[17] Ahrland and Rosengren, *ibid.*, p. 727.

[18] Tichane and Bennett, *J. Amer. Chem. Soc.*, 1957, **79**, 1293.

To the left of the nickel Group of metals the border is not so well defined. Multiple valency is common and many elements occur in both classes according to their oxidation states. In this region the higher valencies tend to class (*a*) character and the low valencies to class (*b*) character, because the *d*-electrons are more available for dative π-bonding the lower the oxidation state. Thus iron(III) in its complexes of high magnetic moment forms very stable complex fluorides and belongs to class (*a*)[15] but iron(0) undoubtedly belongs to class (*b*). All transition metals in their zero-valent states appear to belong to class (*b*). It may be that the metal ions to the left of the nickel Group will best be separated, class (*a*) from class (*b*), by a surface through a three-dimensional arrangement of acceptor atoms which are plotted with their Group numbers as abscissæ, their Period numbers as co-ordinates, and their valencies vertically, so that all under the surface would have class (*b*) character and all above it class (*a*).

Boron is a particularly interesting example of a border element because it does not lie near the typical class (*b*) acceptors associated with Group VIII. Perhaps, together with carbon as acceptor, it may be regarded as a low island of class (*b*) character in a sea of class (*a*) elements.

Data relating to the complex compounds of boron with the heavier ligand atoms are relatively common. These indicate that boron lies on both sides of the border according to its environment in the acceptor molecule and the Group of ligand atoms under comparison. Thus boron trifluoride as an acceptor molecule has class (*a*) character and borine has mild class (*b*) character with all ligand atoms from Groups V and VI in their methyl derivatives. In similar circumstances trimethylborine appears to have mild class (*a*) character with Group V and mild class (*b*) character with Group VI.[19] It seems surprising that boron with no filled *d*-orbitals can have any class (*b*) character at all, and it is probable that the bonding electrons in borine and to a smaller extent in trimethylborine are so weakly held that hyperconjugation occurs, providing weak dative π-bonding to suitable ligand atoms, as Graham and Stone[19] have discussed. Such an explanation is consistent with the existence of the weak carbonyl and phosphorus trifluoride complexes of borine.[20]

In a border-line case such as boron, it can be misleading to take the equilibrium constants K (connected with ΔG) as a measure of the strength of the acceptor-to-donor bond because entropy effects can now make a significant contribution to ΔG. Thus the dissociation constants of the complexes Me_3B,NMe_3 and Me_3B,PMe_3 at 100° are 0·472 and 0·128 respectively,[21] and it appears that the amine complex is the least stable, so trimethylborine is a class (*b*) acceptor. However, the greater dissociation of the amine complex is due to its greater entropy of dissociation ($\Delta S = 45{\cdot}7$) than that of the phosphine complex ($\Delta S = 40{\cdot}0$). The heat of formation, ΔH, of the amine complex (17·6 kcal./mole) is actually greater than that of the phosphine complex (16·5 kcal./mole), indicating that in these analogous

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[19] Graham and Stone, *J. Inorg. Nuclear Chem.*, 1956, **3,** 164 ; and references therein.

[20] Parry and Bissot, *J. Amer. Chem. Soc.*, 1956, **78,** 1524.

[21] Brown, *J.*, 1956, 1248.

complexes the B–N bond is stronger than the B–P bond and that trimethylborine is just on the side of the class (*a*) acceptors.

We shall now consider the relative co-ordinating affinities of the ligand atoms in each Group. Those of Group V are the simplest, followed by Group VII, but Group VI is very complicated and more data are necessary before any general plan will emerge. In this correlation every attempt has been made to keep the comparison as free from extraneous factors as possible. Most weight has been given to unidentate ligands imposing a minimum of steric strain on the system and having ligand atoms as free as possible from conjugation. Both steric and conjugative effects can cause major anomalies. For example, it would be wrong to compare NPh_3 and PPh_3 as typical amines and phosphines. We might wrongly conclude from the existence of PPh_3HI and non-existence of NPh_3HI that the relative affinities of phosphorus(III) and nitrogen(III) for the proton are in the sequence $P > N$ and so that the hydrogen ion has class (*b*) character. Here the nitrogen and the phosphorus atom are not under similar conditions. The compatibility of orbital size between carbon and nitrogen is such that the nitrogen atom is much more strongly conjugated than the phosphorus atom to the benzene nuclei and so in effect loses its lone pair of electrons. It is for this reason that the measurements in Table 2 do not determine whether cadmium is in class (*a*) or (*b*). There is no doubt in the case of silver where the aromatic phosphine, relatively inert amongst phosphines, co-ordinates more strongly than any amine, aliphatic or aromatic.

The Relative Co-ordinating Affinities of Ligand Atoms from Group V.—These ligand atoms in their simplest stable derivatives, the trialkyls, show a simple uniformity of behaviour. With class (*a*) acceptors their co-ordinating affinities lie in diminishing sequence $N \gg P > As > Sb > Bi$, with class (*b*) in the sequence $N \ll P > As > Sb > Bi$. No examples are known from qualitative or quantitative work where any other sequence than $P > As > Sb > Bi$ has even been suggested, and no compound containing bismuth as ligand atom is known. The qualitative and semiquantitative data relating to this Group are summarised in Table 2. Nearly all these are concerned with Group III acceptor atoms and vapour-phase measurements. The examples, except palladium and silver, are all of class (*a*) or have only very weak class (*b*) character, but qualitatively there is no doubt that Pt(II), Cu(I), Au(I), and Au(III) all have very strong class (*b*) character, even stronger than Ag(I).

With class (*b*) acceptors nitrogen with its lower affinity than phosphorus can be placed in the $P > As > Sb > Bi$ sequence, and the position of nitrogen in this sequence will serve as a measure of class (*b*) character. Thus in the case of BH_3, tertiary alkylamines have affinities lying between those of the tertiary phosphines and tertiary arsines, $P > N > As$, connoting definite but weak class (*b*) character. In the case of Ag(I) the amines undoubtedly lie below the corresponding arsines in affinity, $P > As > N$. This appears to be true of all except border-line class (*b*) acceptors, so that the tertiary alkylamines and tertiary alkylstibines compete for third place in the sequence.

Explanatory Note to Tables 2, 4, and 5

Where the first stability constant (log K_1) is given the measurements were made in aqueous solution. Other measurements or ligand displacement reactions were carried out in the vapour phase. Semiquantitative measurements of relative affinities are indicated by symbols and signs, *e.g.*, N > P, etc. Quantitative data are represented by numerical values of ΔH (= heat of dissociation (kcal./mole)) or $1/K_p$ ($t°$) [= association constant (atm.$^{-1}$) at $t°$ c]. The constants arranged horizontally in the Tables are comparable. No account is taken of slight differences in temperature or ionic strengths. V. = very.

Ligands are indicated by superscript letters as follows:

a Methyl derivatives, NMe_3, Me_2O, and MeF and analogues, as appropriate to the reference.
b $3\text{-}NH_2{\cdot}C_6H_4{\cdot}SO_3^-$
c $3\text{-}PPh_2{\cdot}C_6H_4{\cdot}SO_3^-$
d $As(3\text{-}C_6H_4{\cdot}SO_3^-)_3$
e $O(CH_2{\cdot}CO_2^-)_2$
f $S(CH_2{\cdot}CO_2^-)_2$
g $O(CH_2{\cdot}CH_2{\cdot}NH_2)_2$
h $S(CH_2{\cdot}CH_2{\cdot}NH_2)_2$
i $4\text{-}MeO{\cdot}C_6H_4{\cdot}SO_3^-$
j $4\text{-}EtS{\cdot}C_6H_4{\cdot}SO_3^-$
k $4\text{-}PhS{\cdot}C_6H_4{\cdot}SO_3^-$
l $4\text{-}PhSe{\cdot}C_6H_4{\cdot}SO_3^-$
m $NH(CH_2{\cdot}CO_2^-)_2$
n $NH(CH_2{\cdot}CH_2{\cdot}NH_2)_2$
p $4\text{-}NMe_2{\cdot}C_6H_4{\cdot}SO_3^-$
q K = Equilibrium constant in *iso*octane (2 : 2 : 4-trimethylpentane) of the reaction: $(Oct^nNH_2)_2PdCl_2 + PBu^n_3 \rightleftharpoons PBu^n_3,Oct^nNH_2,PdCl_2 + Oct^nNH_2$.

TABLE 2. *Relative affinities of ligand atoms from Group V*

Acceptors		Relative affinities							Ref.
Class (a)		N	>	P	>	As	>	Sb	
$BeMe_2$		N	>	P	>	[As]^a			1
BF_3		N	>	P	>	[As]^a			2
BMe_3	ΔH	17·6		16·5	>	As^a			3, 4
$AlMe_3$		N	>	P^a					5
$GaMe_3$	$1/K_p(100°)$	V. large		33 (130°)		0·75		V. small^a	6
$InMe_3$	ΔH	19·9		17·1	>	As^a			7
Class (b)		N	<	P	>	As	>	Sb	
Pd(II)	log K		3·5^q						8
Ag^+	log K_1	1·23^b		8·15^c		5·36^d			9
Cd^{2+}	log K_1	0·26^b		0·9^c					10
BH_3		N	<	P	$\gg$	As^a			2
$TlMe_3$		N	≈	P	$\gg$	As^a			7

References : [1] Coates and Huck, *J.*, 1952, 4501. [2] Graham and Stone, *J. Inorg. Nuclear Chem.*, 1956, **3**, 164; and references therein. [3] Brown, *J.*, 1956, 1248. [4] Brown, quoted by Chatt, *J.*, 1951, 652. [5] Davidson and Brown, *J. Amer. Chem. Soc.*, 1942, **64,** 316. [6] Coates, *J.*, 1951, 2003. [7] Coates and Whitcombe, *J.*, 1956, 3351. [8] Meddings and Burkin, *ibid.*, p. 1115. [9] Ahrland, Chatt, Davies, and Williams, *J.*, 1958, 276. [10] *Idem, ibid.*, p. 1403.

TABLE 3. *Relative affinities of ligand atoms from Group* VII *

(All figures are log K_1)

Acceptors	Relative affinities						
Class (a)	F	>	Cl	>	Br	>	I
H^+	3·17†		− 7†		− 9†		− 9·5†
Be^{2+}	*ca.* 5		Small				
Mg^{2+}	1·82†		V. small				
Sc^{3+}	7·08†		Small				
La^{3+}	3·56†		− 0·12				
Ce^{3+}	3·99†				0·38†		No complex
Zr^{4+}	9·80†		0·30				
Th^{4+}	8·65†		1·38†				
VO^{2+}	3·30‡		0·04‡				
Cr^{3+}	5·20†		0·60†				
UO_2^{2+}	4·54		− 0·10		− 0·30		
Pu^{4+}	6·77		− 0·24				
Fe^{3+}	6·04†		1·41†		0·49†		
Ni^{2+}	0·66		Small				
Cu^{2+}	1·23†		0·05†		− 0·03†		
Zn^{2+}	0·77		− 0·19		− 0·60		< − 1·3
Ga^{3+}	5·86†		− 0·6†				
In^{3+}	3·78		2·36		2·01		1·64
Sn^{2+}	3·95		1·15		0·73		
Class (b)	F	<	Cl	<	Br	<	I
Pt(II)	< 1§		2·52§		3·04§		4·60§
Ag^+	0·36†		3·04†		4·38†		8·13
Cd^{2+}	0·57		1·59		1·76		2·08
Hg^{2+}	1·03		6·74		8·94		12·87
Tl^+	0·10†		0·68†		0·93†		
			in 4N-$NaClO_4$	→	0·32		0·72
Tl^{3+}			8·1†		9·7†		
Pb^{2+}	< 0·3		0·96		1·11		1·26
Te(IV)	F	<	Cl	<	Br	<	I

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* Compiled from "Stability Constants, Part II", by J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, The Chemical Society, London, 1958, where many more data and original references are given.

† Corrected to zero ionic strength.

‡ Ahrland and Norén, *Acta Chem. Scand.*, 1958, **12** (in the press).

§ log K_1 of the reaction: *trans*-$[C_2H_4,H_2O,PtCl_2] + X^- \rightleftharpoons$ *trans*-$[C_2H_4PtX,Cl_2] + H_2O$ at 25° and an ionic strength of 0·2 ($HClO_4$) (Leden and Chatt, *J.*, 1955, 2936).

TABLE 4. *Relative affinities of ligand atoms from Group* VI

Acceptors		Relative affinities							Ref.
Class (a)		O	>	S		Se		Te	
$BeMe_2$		O	>	[S]^a					1
Ca^{2+}	log K_1	3·4^e		1·4^f					2
BF_3		O	>	S	>	Se^a			3, 4
$AlMe_3$		O	>	S	>	Se	>	Te^a	5, 6
$GaMe_3$	$1/K_p(100°)$	0·93		≈ 0·4		0·66		≈ 0·4^a	5
Zn^{2+}	log K_1	3·6^e		3·0^f					2
Class (b)		O	<	S		Se		Te	
Co^{2+}	log K_1	2·7^e		3·4^f					2
Ni^{2+}	log K_1	2·8^e		4·1^f					2
	log K_1	5·5^g		7·3^h					7, 8
Cu^{2+}	log K_1	3·9^e		4·5^f					2
	log K_1	8·6^g		9·1^h					8
Ag^+	log K_1	− 0·12^i		2·6^j					9
	log K_1			1·7^k		2·6^l			9
				S	<	Se	<	Te^a	5
BH_3		O	<	S	>	Se^a			3
BMe_3		O	<	S	>	Se^a			3
$TlMe_3$		O	<	S^a					10

Footnotes to Table 4 :

References : [1] Coates and Huck, *J.*, 1952, 4501. [2] Tichane and Bennett, *J. Amer. Chem. Soc.* 1957, **79,** 1293. [3] Graham and Stone, *J. Inorg. Nuclear Chem.*, 1956, **3,** 164 ; and references therein. [4] Brown and Adams, *J. Amer. Chem. Soc.*, 1942, **64,** 2557. [5] Coates, *J.*, 1951, 2003. [6] Davidson and Brown, *J. Amer. Chem. Soc.*, 1942, **64,** 316. [7] Gonick, Fernelius, and Douglas, *ibid.*, 1954, **76,** 4671. [8] Lotz, Ph.D. Thesis, Penn. State Univ., 1954. [9] Ahrland, Chatt, Davies, and Williams, *J.*, 1958, 264. [10] Coates and Whitcombe, *J.*, 1956, 3351.

Footnotes to Table 5 *:*

References : [1] Coates and Huck, *J.*, 1952, 4501. [2] Tichane and Bennett, *J. Amer. Chem. Soc.*, 1957, **79,** 1293. [3] Chaberek and Martell, *ibid.*, 1952, **74,** 5052. [4] Lotz, Ph.D. Thesis, Penn. State Univ., 1954. [5] Jonassen, Hurst, LeBlanc, and Meibohm, *J. Phys. Chem.*, 1952, **56,** 16 ; and references therein. [6] Ahrland, Chatt, Davies, and Williams, *J.*, 1958, 276. [7] *Idem, ibid.*, p. 264. [8] Prue and Schwarzenbach, *Helv. Chim. Acta*, 1950, **33,** 985. [9] Graham and Stone, *J. Inorg. Nuclear Chem.*, 1956, **3,** 164; and references therein. [10] Brown and Adams, *J. Amer. Chem. Soc.*, 1942, **64,** 2557. [11] Brown, Bartholomay, and Taylor, *ibid.*, 1944, **66,** 435. [12] Schlesinger and Burg, *Chem. Rev.*, 1942, **31,** 1. [13] Davidson and Brown, *J. Amer. Chem. Soc.*, 1942, **64,** 316. [14] Coates, *J.*, 1951, 2003. [15] Coates and Whitcombe, *J.*, 1956, 3351. [16] Ahrland, Chatt, Davies, and Williams, *J.*, 1958, 1403. [17] Brown, *J.*, 1956, 1248. [18] Stone and Burg, *J. Amer. Chem. Soc.*, 1954, **76,** 386.

TABLE 5. *Relative affinities of ligand atoms from the same Period*

Acceptors		Relative affinities					Ref.
Period II		N	>	O			
$BeMe_2$		N	>	O^{a}			1
Co^{2+}	$\log K_1$	$7\cdot0^{m}$		$2\cdot7^{e}$			2, 3
Ni^{2+}	$\log K_1$	$8\cdot2^{m}$		$2\cdot8^{e}$			2
	$\log K_1$	$10\cdot8^{n}$		$5\cdot5^{g}$			4, 5
Cu^{2+}	$\log K_1$	$10\cdot4^{m}$		$3\cdot9^{e}$			2
	$\log K_1$	$16\cdot1^{n}$		$8\cdot6^{g}$			4, 5
Ag^{+}	$\log K_1$	$0\cdot76^{p}$		$-0\cdot12^{i}$			6, 7
Zn^{2+}	$\log K_1$	$7\cdot0^{m}$		$3\cdot6^{e}$			2, 3
Hg^{2+}	$\log K_1$	23^{n}		$15\cdot8^{g}$			4, 8
BF_3	$1/K_p$	V. large $(177°)^{a}$		$5\cdot8\ (99°)^{a}$			9, 10
BMe_3	$1/K_p$	$2\cdot12\ (100°)^{a}$		V. small $(-78°)^{a}$			9, 11
BH_3	$1/K_p$	V. large $(125°)^{a}$		V. small $(-78\cdot5°)^{a}$			12
$AlMe_3$		N	>	O^{a}			13
$GaMe_3$	$1/K_p$	V. large $(100°)^{a}$		$0\cdot93\ (100°)^{a}$			14
$InMe_3$		N	>	O^{a}			15
$TlMe_3$		N	>	O^{a}			15
		N	<	O			
Ca^{2+}	$\log K_1$	$2\cdot7^{m}$		$3\cdot4^{e}$			2
Period III		P	>	S	>	Cl	Ref.
$BeMe_2$		P	>	S^{a}			1
Ag^{+}	$\log K_1$	$8\cdot15^{c}$		$1\cdot7^{k}$			6, 7
Cd^{2+}	$\log K_1$	$\approx 0\cdot9^{c}$		$0\cdot67^{k}$			16
$\frac{1}{2}B_2H_6$	$1/K_p$	V. large $(200°)^{a}$		$1\cdot56^{*}\ (60°)^{a}$			9
BMe_3	$1/K_p$	$7\cdot8\ (100°)^{a}$		V. small $(25°)^{a}$			9, 17
$AlMe_3$		P	>	S	>	Cl^{a}	13
$GaMe_3$	$1/K_p$	$33\ (130°)^{a}$		$\approx 0\cdot4\ (100°)^{a}$			14
$InMe_3$		P	>	S^{a}			15
Period IV		As	>	Se			
Ag^{+}	$\log K_1$	$5\cdot36^{d}$		$2\cdot6l$			6, 7
BH_3	$1/K_p$	V. large $(80°)^{a}$		V. small $(6°)^{a}$			9, 18
$GaMe_3$	$1/K_p\ (100°)$	$0\cdot75^{a}$		$0\cdot66^{a}$			14
		As	<	Se			
$TlMe_3$		As	<	Se^{a}			15
Period V		Sb	<	Te			
$GaMe_3$	$1/K_p\ (100°)$	V. small		$\approx 0\cdot4^{a}$			14

* $Atm.^{-\frac{1}{2}}$.

The Relative Co-ordinating Affinities of Ligand Atoms from Group VII.—In this Group the simple alkyls, RX, form very few metal complexes analogous to those formed by the trialkyls of Group V and dialkyls of Group VI ligand atoms. The only strongly complexing series of ligands are the halide ions. They are comparatively small and carry a negative charge, and so they are not strictly comparable with the ligands in Tables 2 and 4 containing uncharged co-ordinating atoms from Groups V and VI. The effects of hydration will be more marked. Nevertheless two regular sequences of stabilities of complex halides have been noted.[22–24, 15, 16] With acceptor ions of class (*a*) in aqueous solution the affinities of the halide ions lie in the sequence $F \gg Cl > Br > I$, and with class (*b*) in the sequence $F \ll Cl < Br < I$. This differs from Group V in the occurrence of opposing sequences $Cl > Br > I$ and $Cl < Br < I$. It seems reasonable to suppose that some acceptor near the border between class (*a*) and class (*b*) might form a series of halide complexes of almost identical stabilities and then a mixed sequence could occur, *e.g.*, $F > Cl < Br > I$ or $F < Cl > Br < I$. A vast number of halide complexes have been investigated quantitatively, but only Bi^{3+} shows any tendency to give a mixed sequence.[13] A selection from the large number of data compiled by Bjerrum, Schwarzenbach, and Sillén,[2] together with a few recent additions, is given in Table 3. The values have been chosen to give the best relative affinities of each metal ion for the different halide ions and not of the various metal ions for the same halide ion.

The Relative Co-ordinating Affinities of Ligand Atoms from Group VI.—With metal ions of strong class (*a*) character the sequence $O \gg S > Se > Te$ would be expected since the corresponding sequence is found in both Groups V and VII and this is confirmed with $AlMe_3$ as acceptor (Table 4). With acceptors of class (*b*) almost any sequence of S, Se, and Te might occur since the stabilities of complexes formed by the corresponding elements in Groups V and VII run in opposing sequences, $P > As > Sb$ and $Cl < Br < I$. In fact almost every sequence seems to occur with acceptor atoms of mild class (*a*) to strong class (*b*) character. These are listed in Table 4. Many more data are needed before any rules can be formulated for this Group of ligand atoms, but it seems likely that the data relating to this Group, where sequences depend so much on subtle differences between the acceptor atoms, will be more valuable than any other in classifying the various acceptor molecules and ions according to their co-ordination chemistry.

The Relative Co-ordinating Affinities of Ligand Atoms from the Same Period.—There are few comparable quantitative data relating to ligand atoms in similar circumstances in the same Period, and these are concerned almost entirely with nitrogen and oxygen in Period II (Table 5). There seems little doubt that with all acceptor atoms except the most electropositive the affinities fall, $N > O > F$, in a series of similar ligands, *e.g.*, NR_3, R_2O, and RF. Such a sequence is to be expected wherever covalent donor bonding makes a significant contribution to the strength of the

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[22] Leden, Diss., Lund, 1943, p. 27. [23] J. Bjerrum, *Chem. Rev.*, 1950, **46**, 381.
[24] Ahrland and Larsson, *Acta Chem. Scand.*, 1954, **8**, 354.

co-ordinate bond, because these ligand atoms are all very electronegative and the order is that of rapidly increasing electronegativity and so of decreasing availability of the lone pair of electrons. Further, in combination with class (*b*) acceptors with their filled *d*-orbitals, there will be increasing lone-pair repulsion between the electrons in the *d*-orbitals and the non-bonding lone pairs in the *p*-orbitals of these small ligand atoms, as the lone pairs become more numerous along any series of analogous ligands containing nitrogen, oxygen, and fluorine as co-ordinating atoms. Thus we would expect to find a very rapid decrease in co-ordinating affinity $N \gg O \gg F$ for strong class (*b*) acceptors, a more gradual decrease for border-line acceptors, a slow decrease for the weak class (*a*), and for the very strong class (*a*), *i.e.*, the ions of the most electropositive metals, where the bonding is mainly electrostatic, even a mild reversal of the order to $F > O > N$. The few data available fit with this suggested pattern of co-ordination (Table 5). The expected reversal has been observed with Ca^{2+}.

In Period III, P, S, and Cl, similar arguments hold, but these atoms are more readily polarisable, and their electronegativities are lower and more nearly equal; also because they have vacant 3*d*-orbitals, dative π-bonding becomes possible and lone-pair repulsions should be less. We might therefore expect a similar pattern to that of Period II, but with smaller differences.

In Periods IV and V these trends continue so that the differences between the ligand atoms become small and reversals in the order of the stabilities of their complexes become more probable. In Period V the reversal $As < Se$ appears to occur except with acceptors of moderate to strong class (*b*) character, and in Period VI the reversed order $Sb < Te$ appears to be the rule even with such strong class (*b*) acceptors as platinum [5] and palladium.[25] It is worth noting, in considering the fifth Period, that organic iodides, RI, show some tendency to form complexes, especially to silver(I) [26] which also forms surprisingly strong complexes with dialkyl tellurides.[3]

This Review has concerned itself mainly with the relative affinities of ligand atoms for acceptor atoms under the conditions where complex compounds are formed reversibly, as in the vapour phase or in solution. No attempt has been made to interpret the facts in any except a rudimentary manner, because without more data of bond strengths and heats and entropies of complex formation the interpretation would be largely speculative. Many factors influence the stabilities of complexes but these relative affinities which determine what may be called the compatibility of ligand and acceptor atoms is one of the most important. The regularities which we see emerging from the still very inadequate quantitative data may be summarised as follows:

Acceptor ions and molecules are of two well-defined types: class (*a*), which form their most stable complexes with the first ligand atom in each Group; class (*b*), which form their most stable complexes with the second or a subsequent ligand atom of each Group. In each Group of ligand atoms

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[25] Chatt and Venanzi, *J.*, 1957, 2351.

[26] Andrews and Keefer, *J. Amer. Chem. Soc.*, 1950, **72**, 3113.

the co-ordinating affinities are generally related as follows : Group V, with class (*a*) acceptors, $N \gg P > As > Sb > Bi$; class (*b*), $N \ll P > As > Sb > Bi$; Group VI, with class (*a*), $O \gg S$ and S, Se, and Te variable ; class (*b*), $O \ll S$, and S, Se, and Te variable ; Group VII (halide ions), with class (*a*), $F \gg Cl > Br > I$; class (*b*), $F \ll Cl < Br < I$. When we consider the ligand atoms in Periods, the comparable data are too few to allow definite generalisation. Many more data, especially relating to the heavier ligand atoms, are necessary before any finality will be reached, but tentatively it appears that the affinities run as follows : Period II, with all except the ions of very electropositive metals (*e.g.*, Ca), $N > O > F$ in a similar series of ligands, *e.g.*, NR_3, R_2O, and RF ; Period III, similarly, $P > S > Cl$; Period IV, $As > Se > Br$ and $As < Se < Br$, perhaps about equally distributed amongst acceptors ; Period V, $Sb < Te > I$ with most acceptors, $Sb > Te > I$ rarely, if at all.