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Nephelauxetic and Charge Neutralisation Effects in Post-transition Metal Ions: Comparison with Transition Metal Ions

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The linear relation between Jørgensen's h-function for ligands and the frequencies of s-p electronic tranitions for post-transition $d^{10}s^2$ ions enables the assignment of a number m to these ions which is analogous to k for transition metal ions. m and k allow comparison to be made between $d^{10}s^2$ ions and transition metal ions of the charge neutralisation effects brought about by co-ordination. Results indicate that the uni- and dispositive $d^{10}s^2$ ions, unlike transition metal ions, probably exist in many co-ordination spheres with effective charges which comply with Pauling's electroneutrality principle.

Introduction

The nephelauxetic effect has been studied primarily in transition metal ions.[1] Its occurrence in post-transition metal ions having the $d^{10}s^2$ configuration has been commented upon[2] and it would seem worthy of further study in these ions. For such an investigation it is desirable to compare complexed $d^{10}s^2$ ions with transition metal ions in similar ligand environments. Until recently, the spectral data available have restricted such comparisons essentially to environments provided by the ligands: aquo, chloro, bromo and possibly iodo. However, further data are now available for enviroments provided in 100% phosphoric acid, $NaPO_3$ glass, 97% sulphuric acid, $NaHSO_4$–$KHSO_4$ glass and $2K_2SO_4$–$3ZnSO_4$ glass, spectra having been obtained for the heavier $d^{10}s^2$ ions[3,4,5] (Table I) and for several transition metal ions[6,7] in these media.

Changes in interelectronic repulsion occurring in the patly filled d-shell when a transition metal ion undergoes co-ordination can be expressed by comparing the Racah parameter B for the complex with that for the free ion. The nephelauxetic ratio ($B_{complex}/B_{free\ ion}$) is obtained from optical spectra involving electronic transitions between (for cubic symmetry) e and t_2 orbitals, and is given the symbol β_{35}.

It can be separated into two parameters h and k which are assignable, respectively, to the ligand set and to the central metal ion by the equation,[8,9]

$$(1-\beta_{35})=hk \qquad (1)$$

The ability of a particular set of ligands to bring about orbital expansion of the central metal ion is thus characterised by its h-function. The values of k for the transition metal ions having sufficient data avilable for comparing with $d^{10}s^2$ ions are included in Table II.

For Tl^+, Pb^{2+} and Bi^{3+} it has been shown that the frequency, ν, of the $^1S_0 \rightarrow {}^3P_1$ transition, for the metal ion in various ligand environments bears a linear relationship with h.[5] Data for the corresponding $d^{10}s^2$ ions in the previous period (see Table I) indicate a similar linear relationship. (Furthermore, from the data of the halogeno complexes of Sn^{2+}, Tl^+, Pb^{2+} and Bi^{3+}, there also appears to be a linear relationship with h for the more intense $^1S_0 \rightarrow {}^1P_1$ transition.) Since for the transition metal ions, when h is zero, $B_{complex} = B_{free\ ion}$, it could also be expected for the $d^{10}s^2$ ions that extrapolations of the spectral data to h = 0 would yield values of ν which were equal to the free ion values of the $^1S_0 \rightarrow {}^3P_1$ (and $^1S_0 \rightarrow {}_1P^1$) transition. As seen from Table II, for the uni- and dispositive post-transition metal ions the extrapolated frequencies, ν_f, are close to the experimental frequencies, ν expt.. However, this is not so for Sb^{3+} and Bi^{3+}, the extrapolated values for the $^1S_0 \rightarrow {}^3P_1$ transition being lower than the experimental values by 15 kK for Sb^{3+} and by 19.9 kK for Bi^{3+} (1 kK = 1000 cm^{-1}).

The linear relationship between h and the $^1S_0 \rightarrow {}^3P_1$ transition can be expressed in a form that is analogous with equation 1; viz:

$$(1-\beta_{s-p})=hm \qquad (2)$$

m is a constant peculiar to the post-transition metal ion (values are given in Table II) and β_{s-p} is the s—p *nephelauxetic ratio* (ν_{comlex}/ν_f). (The relationship between h and the frequency of the $^1S_0 \rightarrow {}^1P_1$ transition can be expressed similarly, and the corresponding m values are found to be 0.01 to 0.02 greater).

One important application of this linear relationship is that it enables the h-function of a ligand set

(1) See for example: C.K. Jørgensen, Prog. Inorg. Chem., 1962, 4, 73, and 'Halogen Chemistry'. ed. V. Gutmann Academic Press, London, 1967, pp 313 - 318.
(2) C.K. Jørgensen, 'Absorption Spectra and Chemical Bonding in Complexes', Pergamon Press, Oxford, 1962, p. 187.
(3) J.A. Duffy, S.M. Forbes and M.D. Ingram, J. Chem. Soc. 1970, 451.
(4) J.A. Duffy, and M.D. Ingram, J. Chem. Phys., 1970, 52, 3752.
(5) J.A Duffy and M.D. Ingram, J. Chem. Phys., 1971 54, 443.
(6) J.A. Duffy and W.J.D. Macdonald, J. Chem. Soc., 1970, 977.
(7) J.A. Duffy, Physics and Chem. Glasses, 1972, 13, 65.
(8) Ref. 2, p. 138.
(9) C.K. Jørgensen, 'Oxidation Numbers and Oxidation States', Springer-Verlag, Berlin, 1969, p. 106.

Table I. Frequencies (in kK) of $^1S_0 \to {}^3P_1$ and $^1S_0 \to {}^1P_1$ transitions in $d^{10}s^2$ post-transition metal ions.

	Free Ion	Aquo	Chloro	Bromo	Iodo	100% phosphoric acid	$Na_2O . P_2O$ glass	97% sulphuric acid	$NaHSO_4 . KHSO_4$ glass	$2K_2SO_4 . 3ZnSO_4$ glass
In^+	43.35		33,36	34	32					
	63.03		43	39	41					
Sn^{2+}	55.20		34.7, 38.2	32	28	41.0, 46.0		43.5, 47.5		
	79.91		45.0	41	34.5	—		—		
Sb^{3+}	66.70	42.6?	34.8	27.8		43 sh		42 sh		
	95.95	—	43.9	37.0		—		—		
Tl^+	52.39	46.7	40.5	38.1	35.5	48.2	47.0	48.7, 50.0	48 sh 48.9	47 sh 48.0
	75.66	—	51.0	47.2	43.0	—	—	—	—	—
Pb^{2+}	64.39	48.0	36.8	33.2	27.6	48.2	46.5	50.4	47.8	46.6
	94.34	—	51.0	44.9	—	—	—	—	—	—
Bi^{3+}	75.93	45.0	30.5	26.8	(22.2)	45.0	42.6	43.5	43.5	42.6
	114.60	—	45.0	38.5	27.8	—	—	—	—	—
References		(a)	(a)	(a)	(a)	(b)	(c)	(d)	(d)	(c)

Note: Spectra of Sn^{2+} and Sb^{3+} in H_3PO_4 obtained in this study. References: (a) Ref. 2, Chapter 10; Ref. 8, Chapter 6. (b) Reg. 5. (c) Ref. 4. (d) Ref. 3.

Table II. Value of $\nu_{expt.}$, ν_f (in kK) and m for some post-transition metal ions, and k for some transition metal ions. [a]

Metal ion	$\nu_{expt.}$	ν_f	m	k
In^+ [b]	43.35	44	0.10	
Tl^+	52.39	55.3	0.14	
Sn^{2+} [b]	55.20	55	0.18	
Pb^{2+}	64.39	60.7	0.20	
Sb^{3+}	66.70	52	0.2	
Bi^{3+}	75.93	56.0	0.23	
V^{2+}				0.1
Mn^{2+}				0.07
Ni^{2+}				0.12
Cr^{3+}				0.20
Fe^{3+}				0.24

[a] Transition metal ion data from Ref. 9. [b] The relative incompleteness of data used for In^+ and Sn^{2+} (see Table I) renders only approximate values of ν_f and m.

to be estimated more accurately than it can be from d-d spectra, since shifts in the Rydberg $^1S_0 \to {}^3P_1$ transition are much greater than shifts in d-d spectra. The method of obtaining h from the Rydberg band is especially useful for observing changes in basicity produced by gradual changes in the enviroment of cations in solution (effected by changes in solvent composition, for example), and the application of this to nonaqueous media is discussed elsewhere.[10]

The parameter m is a measure of the extent to which the s and p orbitals are expanded on going from one ligand set of another set of greater h value just as k is the corresponding measure for d orbitals. By interpolation procedures involving the B values of isoelectronic ions in a series of increasing atomic number, Jørgensen[1] has used the values of B_{comlex} for obtaining an effective nuclear charge Z_{min} for co-ordinated transition metal ions. Because of the near linearity between $B_{free\ ion}$ and atomic number, the charge reduction $(Z_o - Z_{min})$ in the metal ion with oxidation number Z_o is approximately equal to hk multiplied by the product of $B_{free\ ion}$ and the rate of change of oxidation number with $B_{free\ ion}$ in the iso-

(10) J.A. Duffy and M.D. Ingram, *J. Amer, Chem. Soc.*, 1971, 93, 6448.

electronic series (in the case of d^5 ions, the frequency of the $^6S \to {}^4G$ transition replaces B). For the transition metal ions relative to the present study, these products have the values: V^{2+}, 4.4; Cr^{3+}, 5.4; Mn^{2+}, 4.6; Fe^{3+}, 5.5; Ni^{2+}, 5.2.

For isoelectronic series of $d^{10}s^2$ ions, $\nu_{expt.}$ for both the triplet and singlet absorptions increases almost linearly with increasing atomic number. (See fig. 1).

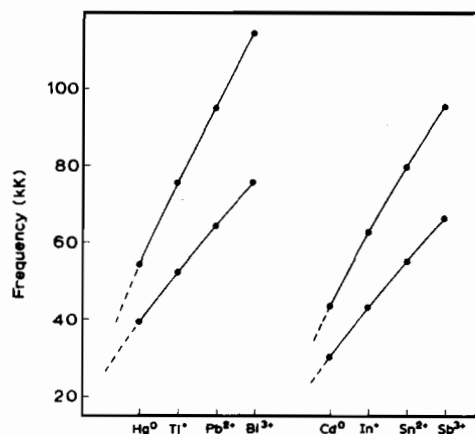Figure 1. Graph showing near-linear relationship between frequency and atomic number for the $^1S_0 \to {}^1P_1$ transition (upper curve) and the $^1S_0 \to {}^3P_1$ transition (lower curve) of $d^{10}s^2$ ions.

Thus a relationship analogous to that for transition metal ions holds for $(Z_o - Z_{min})$, but with m replacing k and $\nu_{expt.}$ replacing B. The products of $\nu_{expt.}$ and the rate of change of oxidation number with ν_{expt} are (based upon the triplet and singlet absorptions respectively): In^+, 3.6 and 3.6; Sn^{2+}, 4.6 and 4.6; Tl^+, 4.1 and 3.8 Pb^{2+}, 5.1 and 4.8; (Sb^{3+} and Bi^{3+} are not included because of the discrepency between ν_f and $\nu_{expt.}$). These values and those for the transition metals given above are within ca. 20% of the mid-range values. It thus follows that the value of $(Z_o - Z_{min})$ for a given co-ordination is influenced chiefly by the magnitude of k or m. $(Z_o - Z_{min})$ for a $d^{10}s^2$ ion will be similar to that for a

Table III. Values of (Z_o-Z_{min}) for metal ions in various co-ordination spheres as obtained from interpolation procedures involving isoelectronic series of free ions (spectral parameters are taken from ref. 11).

Metal Ion	k or m value	97% Sulphuric acid (a)	100% phosphoric acid (b)	Aqueous (a,c)	K_2SO_4-$ZnSO_4$ (2:3) glass (a)	Chloride (c)	Bromide (c)
Mn^{2+}	0.07	0.3	0.3	0.3	0.4	0.5*	0.6*
V^{2+}	0.1			0.6		0.8	
Ni^{2+}	0.12	0.4	0.7	0.6	0.8		
In^+	0.10					0.8	0.9
Tl^+	0.14	0.2	0.3	0.4	0.4	1.0	1.2
Cr^{3+}	0.20	1.2	1.4	1.3	1.8	2.0	
Fe^{3+}	0.24			1.4			
Sn^{2+}	0.18	0.8	1.0			1.7	2.0
Pb^{2+}	0.20	1.1	1.3	1.3	1.5	2.1	2.4

Results obtained for $d^{10}s^2$ ions using data from Table I; for transition metal ions, data is from (a) Ref. 6, (b) Ref. 7, (c) Ref. 9. Where data for aquo-ions conflict the average value is taken. For transition metal ions co-ordination is octahedral except where asterisked when it is tetrahedral.

transition metal ion having k equal to the m value of the $d^{10}s^2$ ion, and this is shown explicitly in Table III. Roughly, the values of m and k are similar when the $d^{10}s^2$ ion is compared with a transition metal ion having an oxidation number one unit greater (Table III), and as a result, the $d^{10}s^2$ ions have values of Z_{min} approximately one unit less than those for the transition metal ions.

Of course the *real* charge decrease brought about by co-ordination will be rather less than that given by $(Z_o - Z_{min})$ since the important contribution due to symmetry restricted covalency has so far been ignored. Although the relative contributions of central field and symmetry restricted covalencies can be approximately assessed for transition metal ions (by measuring β_{35}, β_{33} and β_{55}), this is a much more difficult task for the $d^{10}s^2$ ions, although it is important to note that in considering the nephelauxetic effect for s—p transitions the s—p *orbital* energy difference is invoked, and this is very sensitive to central field covalency. Hence the contribution of symmetry restricted covalency to the nephelauxetic effect for the s—p transition is expected to be somewhat less than it is for d—d transitions, where an orbital energy difference is not involved.

For the transition metals, Jørgensen has shown that if central field and symmetry restricted covalencies make approximately equal contributions to orbital expansion, then in many complexes the transition metal ion has an effective charge lying in the range $+0.5$ to $+2$.[12]

From the above considerations it would appear that, in contrast to the transition metal ions, the uni- and dispositive $d^{10}s^2$ metal ions comply much more closely with Pauling's electroneutrality principle. In other words, when post-transition metal $d^{10}s^2$ ions enter into co-ordination they undergo 'neutralisation' to a much greater extent than do transition metal ions. This would appear to be a continuation of the trend already observed in the transition metal series on the basis of differential ionisation energy parameters.[13]

(11) C.E. Moore, 'Atomic Energy Levels', National Bureau of Standards, 1952.
(12) Ref. 9, p. 111.
(13) Ref. 9, p. 50.