Optical Electronegativity, χ^*, of Transition-metal Ions in Simple Compounds †

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The difference between simple binary compounds and complexes is discussed in the context of charge-transfer (electron-transfer) absorption spectroscopy and correlations involving the optical electronegativities χ^* and χ_{opt}. Using existing data, mainly for binary chlorides and bromides, values of χ^* are obtained for Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}, and applied to binary sulphides and doped zinc sulphide crystals.

Electronic absorption spectroscopy of transition elements has been concerned mostly with d–d transitions, and comparatively little attention has been paid to charge-transfer (c.t.) (electron-transfer) spectra. Furthermore, c.t. spectra have usually been studied for the complex ions of transition elements rather than for their simple binary compounds: for example, oxo-complexes, $[MO_4]^{(8-x)-}$, have received much more attention than the metal oxides, $MO_{x/2}$. The principal reason for this is that electronic states are more straightforwardly dealt with in systems involving discrete energy levels (molecular orbitals) than in systems involving energy bands, which is often the case in simple binary compounds. Also, c.t. absorption is very intense and, because complex ions can often be prepared in dilute solution, obtaining their absorption spectra usually presents no experimental problems, whereas for binary compounds it is necessary to prepare very thin films on optically transparent substrates in order to obtain an absorption spectrum (if the shortcomings of reflectance spectroscopy are to be avoided).

A useful outcome from the study of c.t. spectra of complexes, several years ago, was the correlation of the lowest energy absorption, E, with the optical electronegativity, $\chi_{\text{opt.}}$, of the metal ion and the anion.[1,2] Expressed in electronvolts (eV), the (corrected) energy of the first Laporte-allowed c.t. band is given by equation (1). This energy is designated a

$$E_{\text{corr.}} = 3.72[\chi_{\text{opt.}}(\text{anion}) - \chi_{\text{opt.}}(\text{cation})] \qquad (1)$$

'corrected' energy, $E_{\text{corr.}}$, since in the case of many transition-metal ions it corresponds to a quantity which is the experimentally observed energy, E, minus the change in spin-pairing energy when the electron is transferred to the d level. (Changes in spin-pairing energy can be approximated in terms of the Racah parameter, B, of the complex, and examples for some transition-metal ions are given in Table 1.) If the electron is transferred to the upper d level (e_g for octahedral co-ordination, t_2 for tetrahedral) then Δ must also be subtracted from E. As well as being a useful correlation, the relationship (1) allows an approximate estimate to be made of the energy, E, of the first Laporte-allowed absorption band for any complex, provided the values of $\chi_{\text{opt.}}$ for the cation and anion are known (and also the ligand-field parameters B and Δ if they are required for the correction).

Table 1. Corrections for subtraction from experimental c.t. energies to obtain E_{corr}.

Ion	Configurational change [a]	Spin-pairing energy change [b]	Ligand-field correction [c]	
			Octahedral	Tetrahedral
Cr^{3+}	$d^3 \rightarrow d^4$	$14B$	none	none
Mn^{2+}	$d^5 \rightarrow d^6$	$56B/3$	none	none
Fe^{2+}	$d^6 \rightarrow d^7$	$14B$	none	none
Co^{2+}	$d^7 \rightarrow d^8$	$28B/3$	none	Δ
Ni^{2+}	$d^8 \rightarrow d^9$	$14B/3$	Δ	Δ

[a] For high-spin configurations. [b] From refs. 1 and 2. [c] Δ is the ligand-field splitting parameter.

In transferring from a complex ion to a simple binary compound, *e.g.* from the oxo-complex to the metal oxide mentioned above, we replace the molecular-orbital sequence of energies with an energy-band system. Thus, the electronic transition is no longer transference of the electron from a π-orbital set of the four oxide anions to the e orbital of the metal ion, but instead is transference from the top of the valence band (essentially oxide orbitals) to an orbital belonging essentially to the metal ion, either a discrete orbital or part of the conduction band system. (The effects arising from the change in co-ordination from tetrahedral in the oxo-complex to *e.g.* octahedral in the metal oxide are disregarded for the present.) In a sense, the electronic transition in binary compounds can still be thought of in terms of transferring the electron from the anion to the cation, and, indeed, it has recently been shown that equation (1) holds for simple binary compounds but with optical electronegativities modified to take account of the involvement of energy bands instead of discrete energy levels.[3] To distinguish these optical electronegativities from those of complexes they are designated χ^*. The cations for which χ^* values have so far been obtained are outside the d block and therefore do not require correction for spin-pairing effects or Δ, and $E_{\text{corr.}} = E$. Equation (1) holds well for binary compounds such as NaCl, ZnS, or GaAs where the oxidation number of the cation and anion are equal, but for unequal oxidation numbers, as in Na_3Sb or Al_2S_3, for example, it has been found necessary to subtract 0.6 eV from the value of E calculated by equation (1). (The reason for this correction is not at present understood.) In the absorption spectra of binary compounds and, usually, of complexes, the lowest energy c.t. band is part of a more or less continuous

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† *Non-S.I. unit employed:* eV $\approx 1.60 \times 10^{-19}$ J.

Table 2. Charge-transfer and ligand-field spectral data for some binary compounds of transition metals

Compound	E [a]	Ref.	B [b]	Δ [b]	Ref.	Spin-pairing correction [c]	$E_{corr.}$ [c]
$CrCl_3$	3.90	9	0.069		4	0.97	2.93
$CrBr_3$	3.10	9	0.046		4	0.64	2.46
$MnCl_2$	7.3	10	0.105		4	1.96	5.3
$MnBr_2$	6.3	10	0.103		4	1.92	4.4
$MnS(\alpha)$			0.098		4	1.83	
Mn^{2+} doped in ZnS			0.096		4	1.79	
$FeCl_2$	5.7	10	0.10 [d]			1.4	4.3
$FeBr_2$	4.6	10	0.10 [d]			1.4	3.2
$CoCl_2$	3.9	10	0.096		5	0.90	3.0
$CoBr_2$	3.3	10	0.097		5	0.91	2.4
Co^{2+} doped in ZnS	3.9 [e]	24	0.076	0.46	24	0.71	2.7
$NiCl_2$	4.5	10	0.093	0.94	4	0.43	3.1
$NiBr_2$	3.6	10	0.091	0.91	4	0.42	2.3
Ni^{2+} doped in ZnS	3.1	24	0.069	0.59	24	0.32	2.2

[a] Energy (eV) of lowest energy c.t. absorption from references quoted. [b] In eV, from references quoted. [c] Spin-pairing corrections from Table 1 (also Δ for Ni^{2+} and tetrahedral Co^{2+}) are used for obtaining $E_{corr.}$ as described in the text. [d] Estimated value (see text). [e] Approximate value (see text).

absorption envelope. Thus, equation (1) can be regarded as providing a guide to the onset of intense absorption with increasing photon energy, and is therefore of interest in the context of band gaps.

The purpose of this note is to extend the application of equation (1) to binary compounds of transition-metal ions and to calculate their χ^* values. As in the case of complex ions, the spectroscopic data required include not only the transition energy, E, but also the ligand-field parameters B and, sometimes, Δ. Fortunately, B and Δ can be obtained from single-crystal measurements, since the *d*-configuration terms usually retain their discreteness, and some of the data are in compilations such as refs. 4 and 5. With small values of E, however, *d–d* absorption can be totally obscured, although sometimes fairly good estimates of ligand-field energies can be guessed.

Utilizable spectral data for obtaining E are at present very limited and appear to extend only to Cr^{3+},[6-9] Mn^{2+},[10-18] Fe^{2+},[10,11] Co^{2+},[7,10,14,18,19] and Ni^{2+}.[7,9,10,17-20] What seem the most reliable data (from thin-film transmission and powder reflectance spectra) are collected in Table 2. In all cases, the value of E was assigned in the original literature to the transition from the top of the valence band to the lowest available *d* level of the transition-metal ion. Optical electronegativities of metal ions are often calculated from their halogeno-complexes, usually the chloro- and bromo-ones, and in the present calculations the data of the binary chlorides and bromides are used with the χ^* values of 3.0 for chloride and 2.8 for bromide. Since in these halides the oxidation numbers of the cation and anion are unequal, relationship (2) is used (see above). The

$$E_{corr.} = 3.72[\chi^*(\text{anion}) - \chi^*(\text{cation})] - 0.6 \qquad (2)$$

precision of the data usually allows χ^* to be expressed to no more than 0.05 of a unit. From equation (2), it is apparent that a difference of 0.05 in χ^* corresponds to nearly 0.2 eV in the the value of $E_{corr.}$ However, such precision is usually quite adequate for dealing with, for example, the cut-off of optical transparency.

Calculation of χ^*.—*Chromium*(III). The spin-pairing correction, $14B$, of 0.97 eV for $CrCl_3$ and 0.64 eV for $CrBr_3$ is subtracted from E to yield $E_{corr.} = 2.93$ and 2.46 eV, see Table 2. Substituting these in equation (2) gives $\chi^*(Cr^{III})$ values of 2.05 from $CrCl_3$ data and 1.98 from $CrBr_3$ data.

Manganese(II). Similarly, the spin-pairing correction, $56B/3$, gives the $E_{corr.}$ values shown in Table 2. Equation (2) then yields $\chi^*(Mn^{II})$ values of 1.40 from $MnCl_2$ data and 1.46 from $MnBr_2$ data.

Iron(II). Spin-allowed *d–d* transitions for the high-spin d^6 ion Fe^{2+} do not provide absorption spectra from which B can be calculated. However, since the free-ion B value of Fe^{2+} is close to those of Mn^{2+}, Co^{2+}, and Ni^{2+} (they are all in the range 1.2—1.3 eV), an estimate of $B = 0.10$ eV for both $FeCl_2$ and $FeBr_2$ is reasonable bearing in mind Jørgensen's parametrization of the nephelauxetic effect.[4] The spin-pairing correction is therefore 1.4 eV, and equation (2) then yields χ^* values for Fe^{2+} of 1.68 in $FeCl_2$ and 1.78 in $FeBr_2$.

Cobalt(II). The data in Table 2 give χ^* (Co^{II}) values of 2.03 in $CoCl_2$ and 2.00 in $CoBr_2$. It should be noted that Δ is not involved since the co-ordination of Co^{2+}, which has the high-spin d^7 configuration, is octahedral in both compounds.

Nickel(II). The observed values of E must be reduced by $(14B/3 + \Delta)$, see Table 1. Using the data in Table 2, $\chi^*(Ni^{II})$ is 2.00 in $NiCl_2$ and 2.03 in $NiBr_2$.

Discussion

The agreement between χ^* values obtained for the chlorides and for the bromides is good, and the average values for the cations are given in Table 3. It is a pity that more data are not available to increase the reliance of these values, but this shortcoming often accompanies the obtaining of optical electronegativities. Table 3 also contains the Pauling electronegativities relevant to the dipositive ions, and it can be observed for both types of electronegativity that there is an increase with increasing atomic number until the 3*d* level is completed at Zn^{2+} when there is a marked decrease. It should be noted that the χ^* electronegativities are for the ions in octahedral co-ordination.

The use to which χ^* values can be put is very limited at present owing to the small number of ions for which this parameter has been determined. For non-transition-metal ions, χ^* electronegativities can be used, in conjunction with equation (1) or (2), to predict the band gap of binary sulphides, selenides, arsenides, *etc.*,[3] and thus the onset of intense optical absorption. This is illustrated by the sequence CdTe, ZnTe, CdS, ZnS, for which the experimental (and predicted) band gaps are 1.6, 2.4, 2.6, and 3.9 eV respectively. The colours are black, red, yellow-orange, and white, which makes

Table 3. Pauling and χ^* electronegativities of transition-metal ions

	Cr^{3+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
χ^* electronegativity	2.0	1.45	1.75	2.0	2.0		1.1 [a]
Pauling electronegativity		1.55	1.83	1.88	1.91	2.0	1.65

[a] From ref. 3.

good sense when it is borne in mind that the visible range of the spectrum is roughly 1.6—3.0 eV.

There are important technological devices whose development would be greatly assisted by the facility to predict optical transparency or absorption in binary compounds. Examples of such devices include electrochromic display screens and electrochromic mirrors and windows which rely upon an electric field bringing together (and dispersing) ions that constitute systems absorbing strongly in the visible region. In the selection of suitable cations and anions for these systems it is obviously necessary to know the light absorbing properties of the final ' product ', but if this had not been isolated previously, for reasons such as atmospheric attack (from which it could be protected in the electrolysing medium), then its appearance would be unknown. Clearly, the ability to predict the onset of optical absorption would be very useful.

As an illustration of this application, we refer to the sulphides ZnS, MnS, CoS, and NiS. Their colours (white, buff, black, and black, respectively) are, in fact, familiar as precipitates in qualitative analysis. χ^* for sulphide is 2.15,[3] and hence the values of $E_{\text{corr.}}$ $\{= 3.72[2.15 - \chi^*(\text{cation})]\}$ are 3.9 eV for ZnS, 2.6 eV for MnS, and 0.6 eV for both CoS and NiS. These values must be adjusted in the usual way, except in the case of ZnS, the optical spectrum of which should be clear for photon energies up to *ca.* 3.9 eV. For adjusting the $E_{\text{corr.}}$ value of MnS it is fortunate that the ligand-field spectrum is known, and the B value (Table 2) gives a spin-pairing energy of $56B/3 = 1.8$ eV, and hence the predicted value of E is 4.4 eV. Thus, as in the case of ZnS, the onset of intense optical absorption should not occur until the u.v. region of photon energies is reached. (Slight optical absorption occurs in the visible region for MnS owing to spin-forbidden *d–d* transitions.) For CoS and NiS, B is not known, but can be guessed from the data for Co^{2+} and Zn^{2+} doped in ZnS (Table 2); also, Δ for octahedral Ni^{2+} can be taken roughly as twice that for Ni^{2+} doped in ZnS. However, with $E_{\text{corr.}}$ amounting to only 0.6 eV for both compounds, the corrections are probably not significant. With such a small separation between the valence band and the *d* level, it is probable that the *d* orbitals no longer exist as discrete energy levels, but are involved in the energy-band system. This will reduce drastically the adjustments necessary for $E_{\text{corr.}}$. Thus, the onset of optical absorption will occur at energies just above $E_{\text{corr.}}$, corresponding to the observed black colour of these compounds.

It is possible to prepare Co^{2+} and Ni^{2+} as dilute CoS_4 and NiS_4 tetrahedral chromophores in crystals of ZnS doped with these ions. There is a distinct difference in appearance between the dilute systems, Co^{2+} and Ni^{2+} doped in ZnS, and the black binary sulphides CoS and NiS, since the former are devoid of extensive c.t. absorption in the visible region and are therefore transparent (although coloured owing to *d–d* absorption which yields spectra from which B and Δ in Table 2 are evaluated). Since the $\chi_{\text{opt.}}$ values of tetrahedrally co-ordinated Co^{2+} and Ni^{2+} (1.9 and 2.05, respectively[2,21]) are fairly close to the χ^* values of these ions given in Table 3, it follows that $\chi_{\text{opt.}}$ for sulphide in the CoS_4 and NiS_4 chromophores must be significantly greater than the χ^* value of 2.15 which is obtained for sulphide in the ZnS crystal. This implies, surprisingly, that the Co^{2+} and Ni^{2+} ions must be regarded as isolated ions in the crystal and not as pseudo-Zn^{2+} ions: Co^{2+} and Ni^{2+} are ' central ions ' with a co-ordination sphere consisting of four sulphide ions (ligands) that are polarized by Zn^{2+} ions. The effect of polarization on optical electronegativity has previously been discussed,[22] and although it is small for most ions, it is exceptionally large for the O^{2-} ion, and it might be expected also to be pronounced for the S^{2-} ion. Along the lines of previous arguments and observations,[22] it seems likely that the effect of polarization upon sulphide would be to increase its optical electronegativity.

Since ZnS is an important host medium for metal ions, it is worthwhile obtaining the $\chi_{\text{opt.}}$ value for sulphide in the chromophoric sites provided by ZnS. For Ni^{2+} doped in ZnS the energy for transferrring an electron from the top of the valence band to the *d* level has been calculated as 2.458 eV at 77 K,[23] but the experimentally measured absorption maximum is at 3.0—3.1 eV.[24,25] For Co^{2+} doped in ZnS the absorption maximum has not been obtained owing to the growing absorption of the ZnS host, but the absorption envelope suggests that compared with Ni^{2+} doped in ZnS it is blue shifted by *ca.* 0.8 eV.[24] Taking into account the spin-pairing energies and also Δ, $E_{\text{corr.}}$ has the value 2.7 eV for Co^{2+} doped in ZnS and 2.2 eV for Ni^{2+} doped in ZnS, thereby indicating (from both sets of data) a $\chi_{\text{opt.}}$ of 2.6.

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