

IR spectroscopic study of some oxine transition metal complexes

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The IR absorption spectra of oxine and their transition metal (Mn^{++} , Co^{++} , Ni^{++} , Cu^{++} , Zn^{++} , Cr^{++} , Cr^{+++} and Fe^{+++}) complexes were recorded in the region 200 to 2000 cm^{-1} and are discussed. It can be assumed that the transition metal oxine complexes are of higher symmetry and hence only two metal-ligand (ML) bands appear. The intensity of the ML bands was calculated by computer. It was found that the intensity of these bands forms the sequence: $Mn^{++} < Co^{++} < Ni^{++} < Cu^{++} > Zn^{++}$, which is the same as that for a tetrahedral high spin CFSE.

1. Introduction

In previous work considerable attention has been paid to the interpretation of the IR absorption spectra of complex organic compounds [1-7]. Interest has centred principally on attempts to associate absorption bands at a specific frequency with the presence of certain groups in the molecule. Some workers have reported the IR spectra of the metal chelated compounds. Cardwell and Magee [8, 9] have studied the IR spectra of metal oxine complexes prepared by different methods. The metal-ligand vibrations have become a subject of some controversy. Gordon and Magee [10] have assigned the band appearing at 732 cm^{-1} to M-O stretching vibration. Larsson and Backillson [11] have shown that the band at 490 cm^{-1} is due to M-N stretching vibration in trisoxinato aluminium, iron and cobalt. Clark *et al.* [12] and Goldestein *et al.* [13] have shown that the M-N vibration in pyridine and quinoline complexes of some divalent metal ions lie in the region of 260 cm^{-1} . In previous work [14] the M-O stretching vibration was assigned at $485 \pm 5 cm^{-1}$. Hullet *et al.* [15] also assigned the M-O stretching vibration at 460 to 560 cm^{-1} and the M-N vibration appeared in the 300 cm^{-1} region. Hassan *et al.* [16] assigned the M-O stretching vibration at 325 cm^{-1} and M-N vibration at 290 cm^{-1} .

This work aims to investigate the IR spectra of some transition metal oxine complexes in the range 200 to 2000 cm^{-1} . The metal-ligand stretching vibration frequency will be assigned and discussed. The intensity of the ML band has been calculated which will throw light upon the structure of these complexes.

2. Experimental technique

The different metal chelates were prepared according to the procedure given by Charles *et al.* [17]. The IR spectra were carried out using a Beckman 4250 spectrophotometer. The spectrum obtained is automatically recorded on a paper whose scale is in

percentage transmittance against wavenumber in cm^{-1} . The IR spectra of these complexes are obtained in a potassium bromide (KBr) disc used as a reference. The measurements were made at room temperature (20°C). The frequencies of the bands are reproducible to $\pm 1 cm^{-1}$.

3. Results and discussion

The infrared absorption spectra of oxine and their transition metal complexes are shown in Figs 1a and 1b. Assignments of the absorption bands are shown in Table I. If the spectra of the metal-ligand complexes are compared with those of the ligand, it is interesting to notice that the new bands at 405 ± 12 and $504 \pm 17 cm^{-1}$ appearing in the case of all the chelated compounds are not found in the spectra of the ligand (oxine). The position of these bands are found to be metal sensitive and to be strongly dependent on the metal ion. These two bands show a high dependence on the number of 3d electrons, Fig. 2a. In this respect, the order of change in the band position form the sequence $Mn < Co < Ni < Cu > Zn$. In other words, it assumes the Irving-Williams sequence of stability constants which also reflects the CFSE in a tetrahedral environment [18]. Fig. 2b shows the relation between the absorption frequency and the ionic radius of the metal ion. From this figure, it can be seen that, as the ionic radius decreases the frequency increases. This means that these bands at $405 \pm 12 cm^{-1}$ and $504 \pm 17 cm^{-1}$ are due to M-N and/or M-O stretching vibrations. The frequencies of these two bands increase linearly with increasing atomic weight as shown in Fig. 2c. The contradiction observed in this case can be explained on the basis of the other factors which must be taken into account, the band length in particular. Further, it could be suggested that the electrostatic interaction between the metal ion and the ligand is the factor determining the variation in the force constant rather than the atomic weight of each metal. Thus it can be concluded that these two

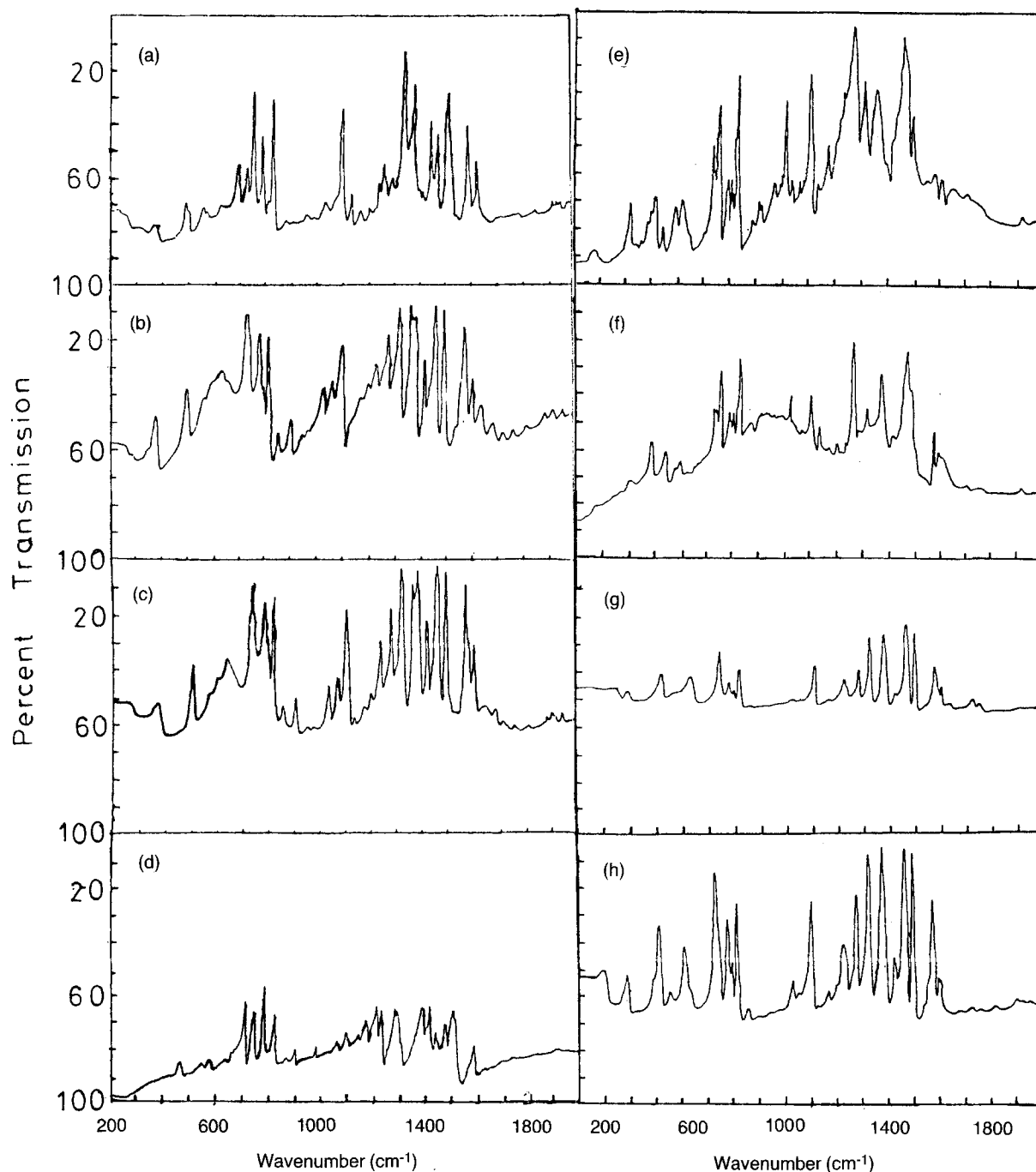


Figure 1 IR absorption spectra of oxine and their transition metal complexes. (a) Ni(OX)₃, (b) Co(OX)₃, (c) Mn(OX)₃, (d) OX, (e) Cu(OX)₃, (f) Zn(OX)₃, (g) Cr(OX)₃, (h) Fe(OX)₃.

bands are due to M–N and M–O vibration. These two bands (ML) are found to exhibit a frequency variation with the variation of CFSE of a tetrahedral high spin, Fig. 2d. Thus, the spectra of these complexes exhibit a similar order of sensitivity to the CFSE and therefore similarly assigned.

The carbon–oxygen (C–O) vibration bands at $1108 \pm 4 \text{ cm}^{-1}$ show a frequency change because of the change of electronic distribution in the environment of the C–O band in chelation. This band is largely affected with the physical properties of the cation as shown in Figs 3a, 3b, 3c and 3d. This indicates that the electronic distribution of the molecule specially in the neighbourhood of the C–O bond is greatly affected by chelation.

The absorption bands in the region of 1630 to 1400 cm^{-1} of C=N and C=C stretching vibration are

mostly shifted to lower frequencies in the spectra of the metal complexes than the respective bands in oxine (Table I). This shift could be explained on the assumption that, on chelation, the electron distribution of the quinoline ring is slightly disturbed and partially contributes to chelation.

As a confirmation, the integrated intensity of the ML bands was calculated according to the Dweius and Thomson equation [19]

$$A = \frac{\pi a}{2W} \int_{\nu_1}^{\nu_2} D(\nu) d\nu$$

where A is the integrated intensity, W the weight of the solute in the disc, a its surface area, $D(\nu)$ the optical density and ν the wavenumber. The calculations in each case were taken as an average of five different measurements. The intensities of these

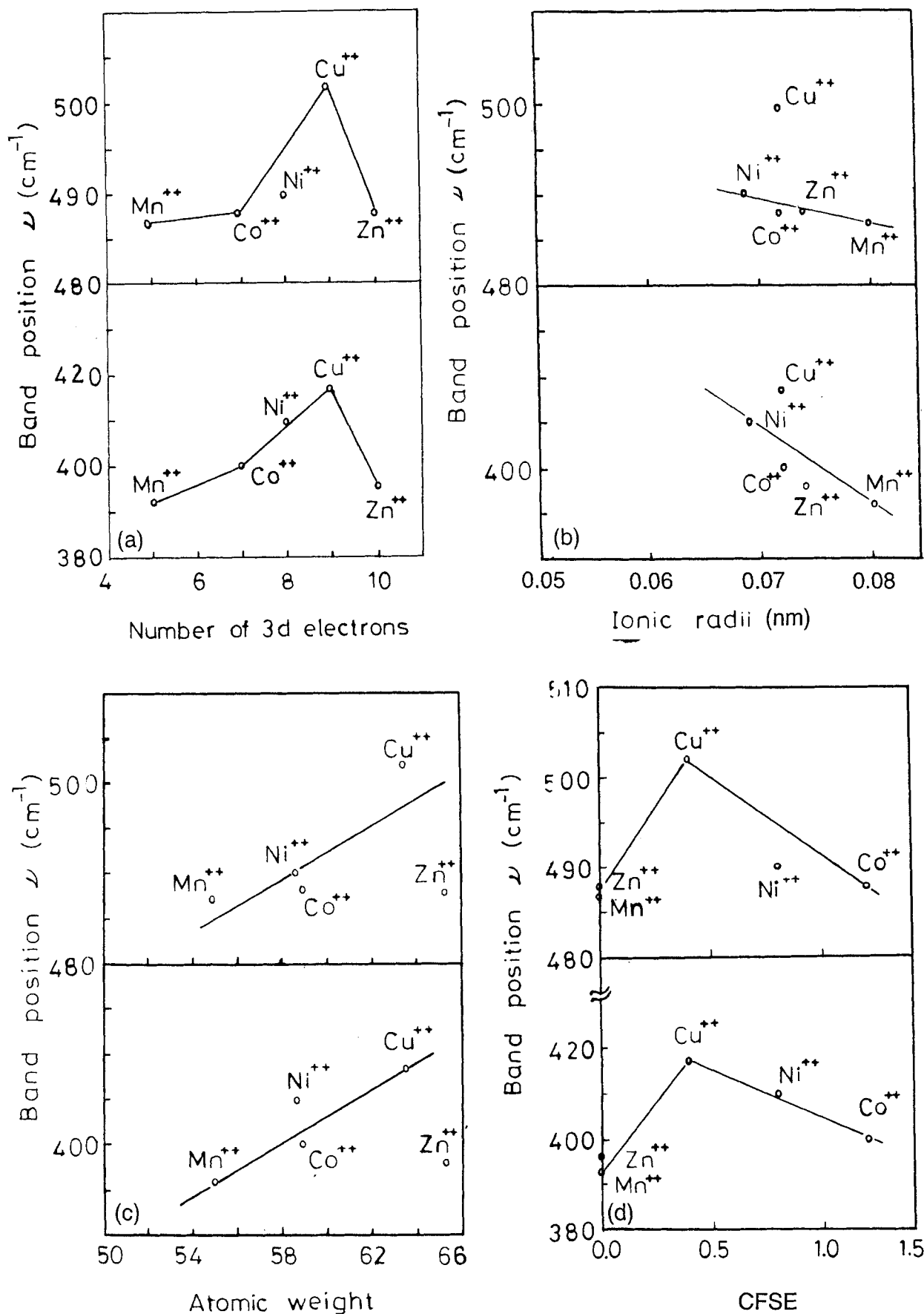


Figure 2 (a) Relation between band position and number of 3d electrons. (b) Relation between the ML band position and ionic radii. (c) Relation between the ML band position and atomic weight. (d) Relation between the ML band position and CFSE.

bands form the sequence $\text{Mn}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$; $\text{Fe}^{3+} < \text{Cr}^{3+}$. It was found that the intensities of the ML bands depend on the metal ion. From Fig. 4a it can be seen that the intensity

increases with decreasing ionic radius of the metal ion. This means that the integrated band intensity is inversely proportional to the bond distance. From Fig. 4b it can be concluded that the intensity increases

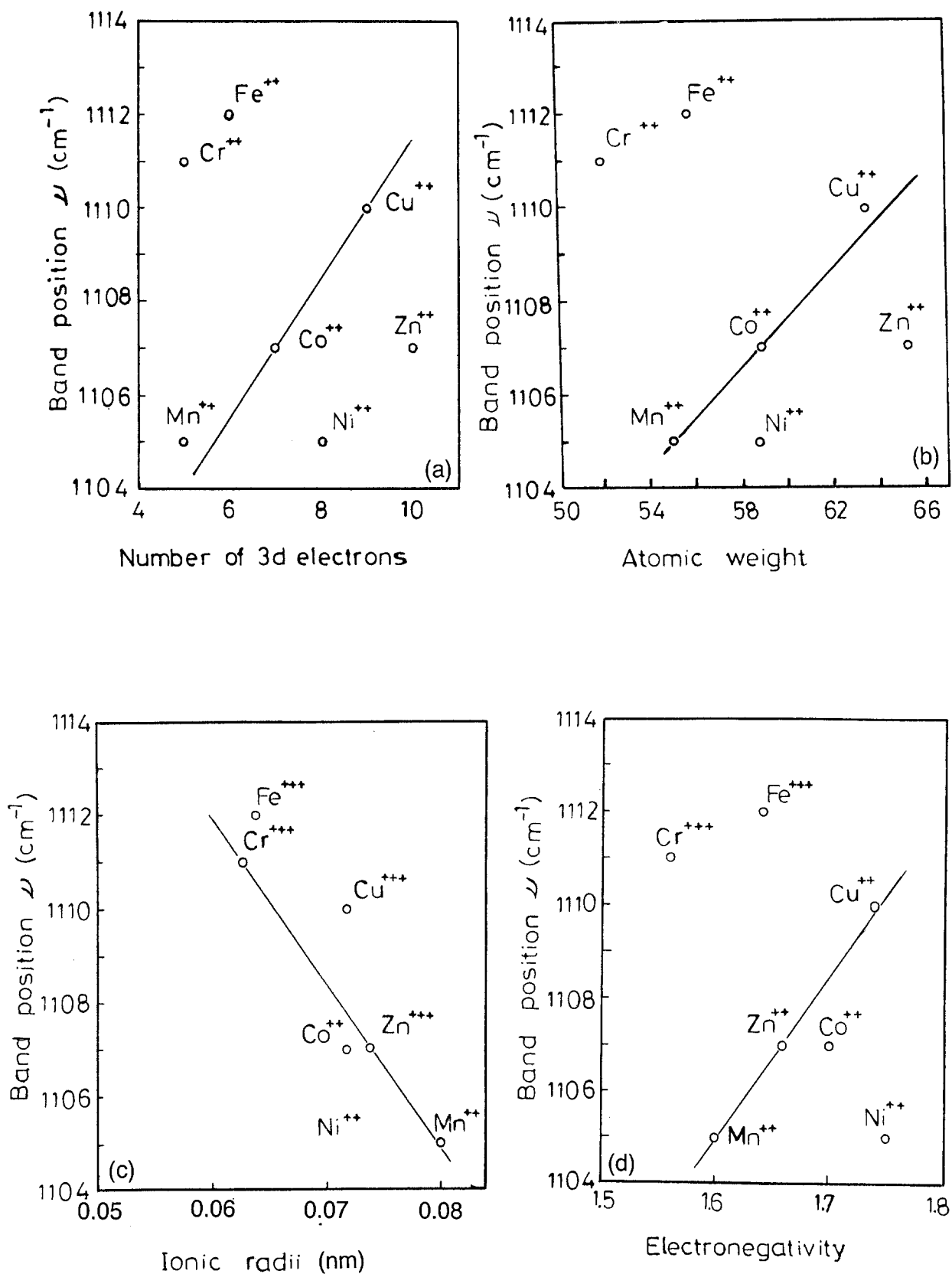


Figure 3 (a) Relation between the C-O band position and number of 3d electrons. (b) Relation between the C-O band position and atomic weight. (c) Relation between the C-O band position and ionic radii. (d) Relation between the C-O band position and electronegativity.

as the frequency or the force constant increases. This means that the intensity increase is due to the increase in covalency. The ML bands show intensity variation with CFSEs of a tetrahedral high spin configuration (Fig. 4c) which is qualitatively parallel to the variation in the 3d orbital population of the metal ion.

From the previous discussion it can be concluded that these complexes are of tetrahedral structure.

Nakamoto *et al.* [20] suggested that metal chelates 1 : 2 compounds show for IR(ML) bands in the case of tetrahedral structure. In the present work, only two IR bands appeared in the region from 250 to 550 cm^{-1} and were assigned as metal-ligand vibration bands as previously mentioned and confirmed. This can be explained assuming that the transition metal oxine complexes under investigation probably possess

TABLE I IR spectra of some transition metal oxinate in the 2000 to 200 cm⁻¹ region

Oxine	Mn ⁺⁺	Co ⁺⁺	Ni ⁺⁺	Cu ⁺⁺	Zn ⁺⁺	Cr ⁺⁺⁺	Fe ⁺⁺⁺	RI	Assignment
1627	1602	1625	1603	1610	1605	1605	1610	W	C=N Stret.
1595	-	-	-	-	-	-	-	W	C=C Stret.
1582	1572	1582	1587	1585	1583	1572	1580	S	C=C Stret.
1504	1495	1493	1503	1505	1480	1498	1495	V.S	C=C Stret.
1473	1464	1470	1470	1473	1452	1465	1462	V.S	C=C Stret.
1435	-	-	-	-	-	-	-	-	C=C Stret.
1412	1418	1425	1422	1404	-	1422	1426	M	C=C Stret.
1382	1382	1380	1376	1380	1380	1375	1384	S	ring C-H bending
-	1313	1330	1325	1316	-	1322	1375	S	C-N
1283	1265	1268	1283	1276	1270	1280	1268	S	C=C Stret.
1225	1230	1222	1224	1240	1240	1235	1242	Sh	C-N
1208	1202	1207	1208	1208	1206	1222	-	W	C-C ring Sket.
1168	1168	1178	1175	1178	1176	1170	1184	M	O-H bending
1140	1132	1142	1136	1137	1138	-	1140	M.Sh	C-H bending
-	1105	1107	1105	1116	1107	1111	1112	V.S	C-O Stret.
1095	-	-	-	1094	-	1087	-	Sh	O-H bending.
1060	1060	1068	1066	1066	1067	1050	1060	W	O-H bending.
1030	1030	1023	-	1035	1022	1030	1035	M	O-H bending.
-	-	-	1015	-	-	-	-	V.S	C-O
975	-	-	-	972	-	-	-	M	C-H deform.
898	902	895	905	913	870	871	918	W	C-H deform.
820	818	829	824	815	828	822	835	S	C-C deform.
808	800	810	802	807	802	802	810	M	C-C deform.
784	782	787	782	795	785	783	783	S	C-H out of plane deformation.
743	738	755	750	763	754	743	733	V.S	C-H out of plane deformation.
711	724	727	728	738	738, 728	-	745	S	C-H out of plane deformation.
670	665	668	668	671	665	-	-	Sh	C-H out of plane deformation.
635	635	628	630	623	625	610	613	W	C-H out of plane deformation.
575	574	545	544	598, 552	543	-	533	S	
-	487	488	490	502	487	522	509	S	(M-O) Stret.
465	-	-	-	-	-	-	-	M	
-	392	400	410	417	396	398	415	M	(M-N) Stret.
270	270	275	260	280	270	-	305		

RI: Relative Intensity; W: Weak; M: Medium; S: Strong; VS: Very Strong, Sh: Shoulder.

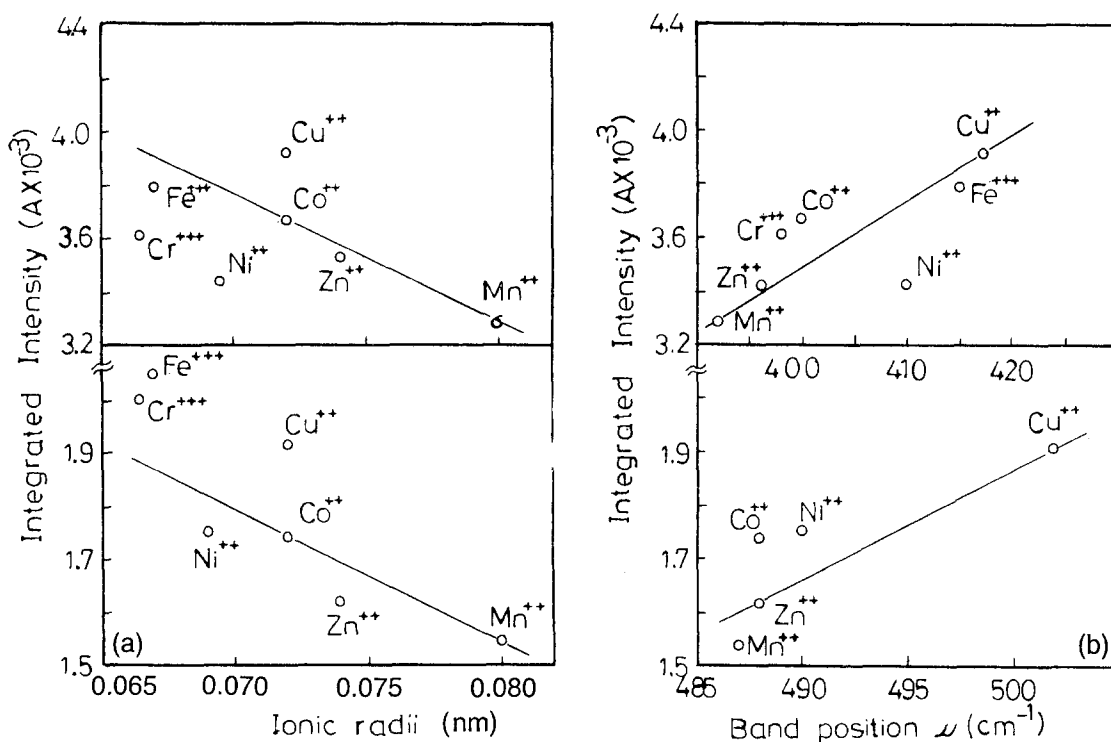
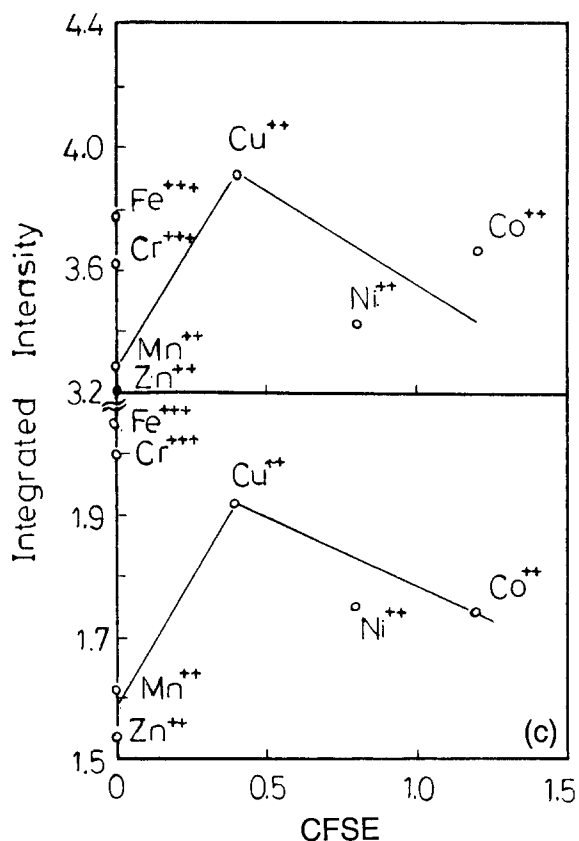


Figure 4 (a) Relation between the integrated intensity and ionic radii. (b) Relation between the integrated intensity and band position. (c) Relation between the integrated intensity and CFSE.



higher symmetry and only two metal-ligand (ML) bands appear.

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