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TEMPERATURE–ELECTRICAL CONDUCTIVITY RELATIONS FOR 5-NITRO- AND 6-NITROBENZIMIDAZOLE AND THEIR TRANSITION METAL COMPLEXES

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ABSTRACT

The electrical conductivities of a new series of some transition metal complexes of 5-nitro- and 6-nitrobenzimidazole, L^1 and L^2, respectively, have been investigated as a function of temperature, anion, metal ion and bulkiness of the imidazoles. The conductivity data measured in the temperature range 298–388 K were correlated to the geometrical change. Empirical equations have been constructed to correlate the variation of the activation energy, ΔE (eV), with log σ_0.

INTRODUCTION

Imidazoles have attracted much interest and are of considerable importance as versatile ligands. This is due to their anti-microbial activity [1] and their radiotherapeutic properties [2]. These compounds have been found to be important in biological activities, for example, in the histidyl residue of proteins and as potential fungicides [3–6]. Electrical conductivity is an important physical property of solids not only for practical applications, but also to interpret various physical phenomena [7–14]. In this article, the electrical conductivities of some transition metal complexes of 5-nitro- and 6-nitrobenzimidazole in the temperature range 298–388 K are investigated.

EXPERIMENTAL

The 5-nitro- and 6-nitrobenzimidazole were purchased from Sigma Chem., Inc.

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All metal complexes were prepared and identified as previously reported [15–20]. The complexes have the stoichiometry 1 : 2.

The electrical conductivity was measured in the temperature range 298–388 K. The samples were prepared as tablets at a pressure of 12 tons cm^{-2}. The tablets were 10 mm in diameter and had a thickness of 0.3–0.5 mm. The tablets were covered on both sides with silver paste to improve the contact with the measuring electrodes. Each sample was maintained between two copper electrodes in a holder especially designed for this purpose. The temperature was controlled from 298 to 388 K with a stability and an accuracy of ± 0.1 K. The temperature was measured using a pre-calibrated Cu–constantan thermocouple attached to the sample. The electrical conductivity was measured by applying a stabilised d.c. voltage across the sample and measuring the potential difference across a standard 1 Ω resistor connected in series with the specimen.

RESULTS AND DISCUSSION

The electrical conductivity of the imidazoles and their metal complexes are shown as a function of the absolute temperature in Figs. 1–4. The conductivity was found to have a magnitude of the order $10^{-6}\ \Omega^{-1}\ cm^{-1}$. This is close to the conductivity of semiconductors [7–14]. The conductivity data vary exponentially with the absolute temperature according to the Arrhenius relation

$$\sigma = \sigma_0 e^{-\Delta E/2kT} \tag{1}$$

where σ is the electrical conductivity, σ_0 is the preexponential term, and ΔE, k and T have their usual meanings.

The small changes in σ in the lower temperatures portions of the plots are a reflection of the ΔE values, see Table 1, and can probably be explained on the basis of a simple single-band model. Straight lines are obtained when ΔE is plotted against log σ_0, see Figs. 5 and 6. Using least-squares analysis, the following empirical equations were deduced to correlate ΔE and log σ_0.
For 5-nitrobenzimidazole metal complexes: $\Delta E = 0.078 \log \sigma_0 + 0.43$ for chlorocomplexes; and $\Delta E = 0.047 \log \sigma_0 + 0.31$ for acetatocomplexes.
For 6-nitrobenzimidazole metal complexes: $\Delta E = 0.047 \log \sigma_0 + 0.25$ for chlorocomplexes; and $\Delta E = 0.051 \log \sigma_0 + 0.32$ for acetatocomplexes.

On plotting ΔE against log σ_0 for complexes having the same metal ion, Cu^{II} or Cd^{II}, the same ligand (L^1 or L^2) but with different anions (Cl^-, Br^-, OAc^- or SO_4^{2-}), straight lines are obtained, see Fig. 6. From these plots, the following empirical equations were deduced:
For copper(II) complexes: $\Delta E = 0.049 \log \sigma_0 + 0.30$ for 5-nitrobenzimidazole complexes; and $\Delta E = 0.066 \log \sigma_0 + 0.25$ for 6-nitrobenzimidazole complexes.

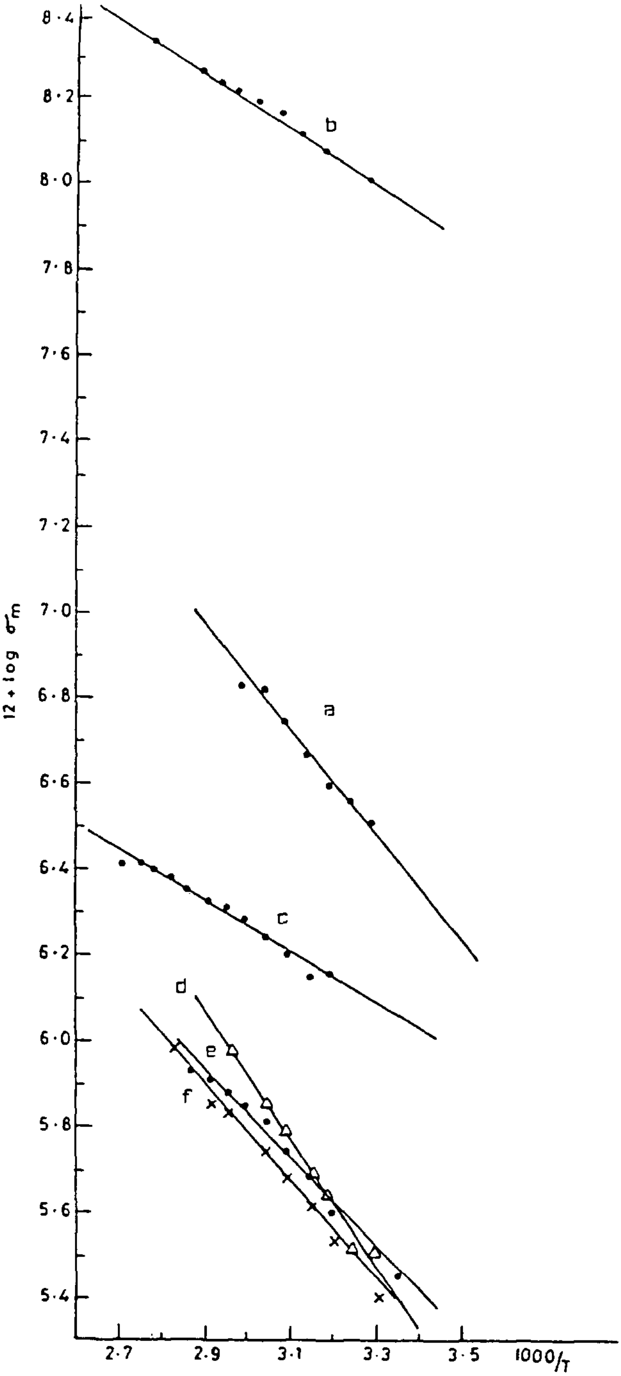

Fig. 1. Electrical conductivity data for: (a) 5-nitrobenzimidazole (L^1) ligand, (b) CuL_2Cl_2 complex, (e) NiL_2Cl_2 complex, (c) CoL_4Cl_2 complex, (f) CdL_2Cl_2 complex and (d) ZnL_2Cl_2 complex.

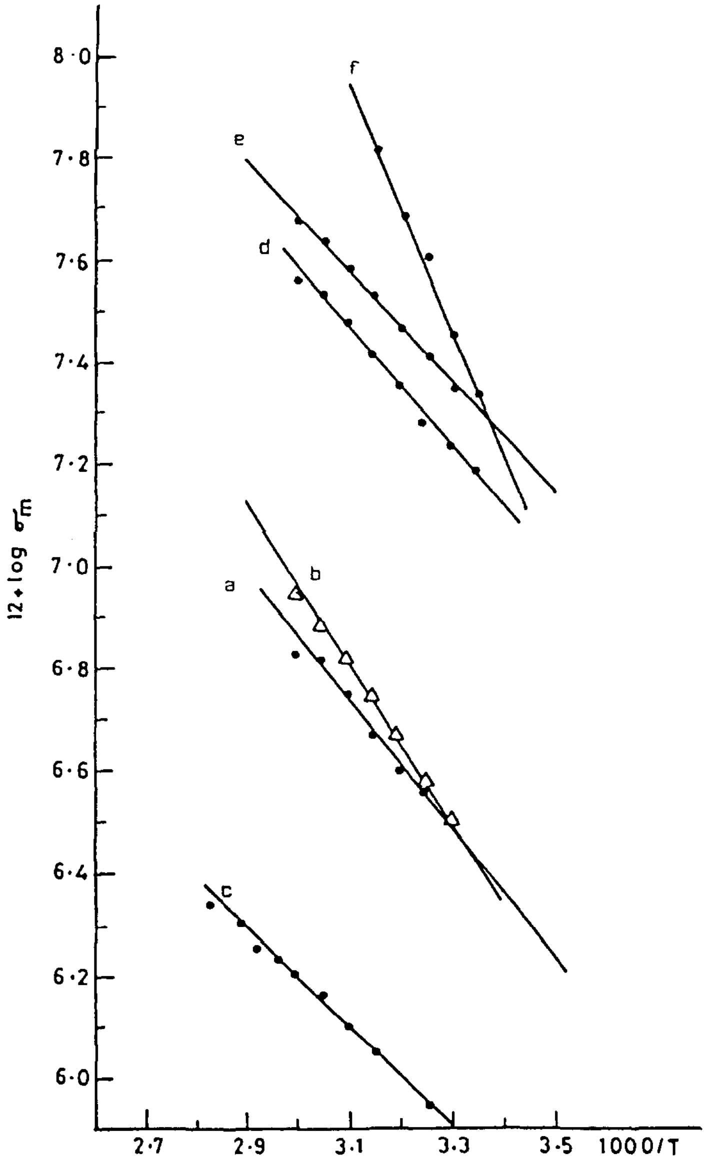

Fig. 2. Electrical conductivity data for: (a) 5-nitrobenzimidazole (L^1) ligand, (b) $NiL_2(OAc)_2$, (c) $CdL_2(OAc)_2$, (d) $ZnL_2(OAc)^2$, (e) $CoL_4(OAc)_2$ and (f) $Cu_2L_2(OAc)_2$.

For cadmium(II) complexes: $\Delta E = 0.041 \log \sigma_0 + 0.33$, for 5-nitrobenzimidazole complexes; and $\Delta E = 0.057 \log \sigma_0 + 0.31$, for 6-nitrobenzimidazole complexes.

From the above data, the following conclusions may be drawn.

(1) Some of the complexes possess lower electrical conductivities and activation energy values than those of the free organic compounds. This could be attributed to the scattering mechanism and/or to the polymeric

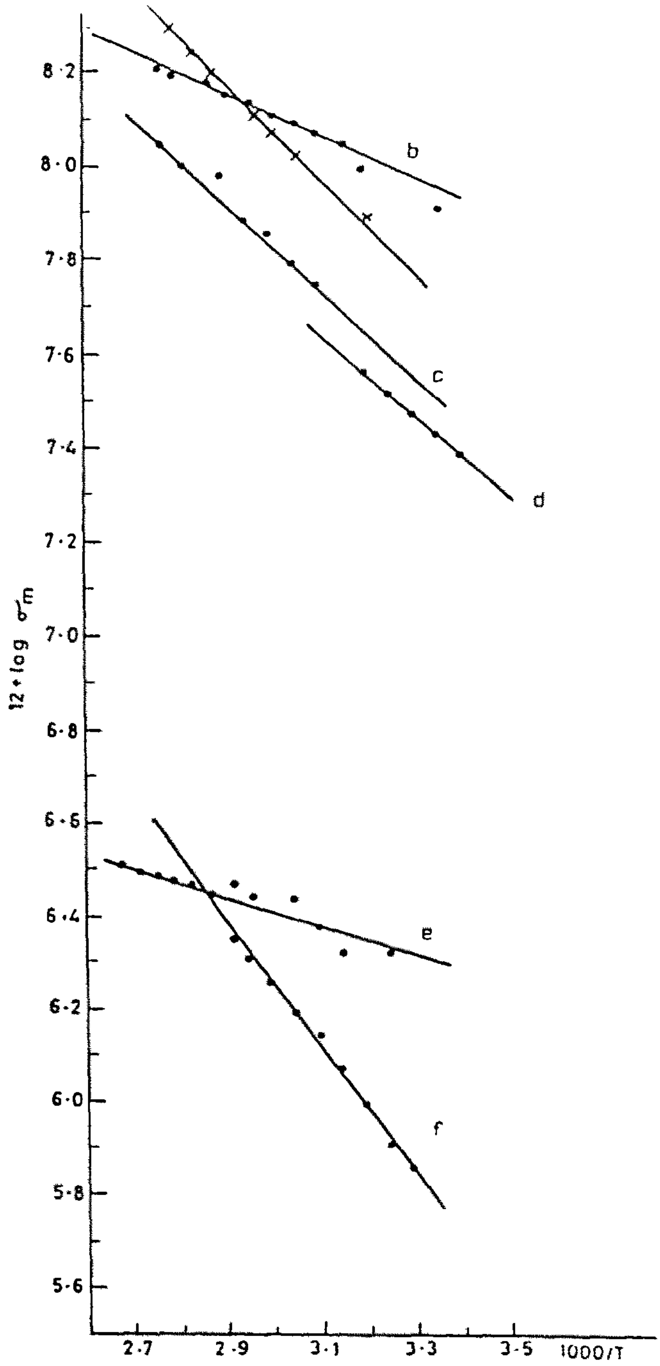

Fig. 3. Electrical conductivity data for: (a) 6-nitrobenzimidazole (L^2), (b) CdL_2Cl_2, (c) ZnL_2Cl_2, (d) CuL_2Cl_2, (e) NiL_2Cl_2 and (f) CoL_4Cl_2.

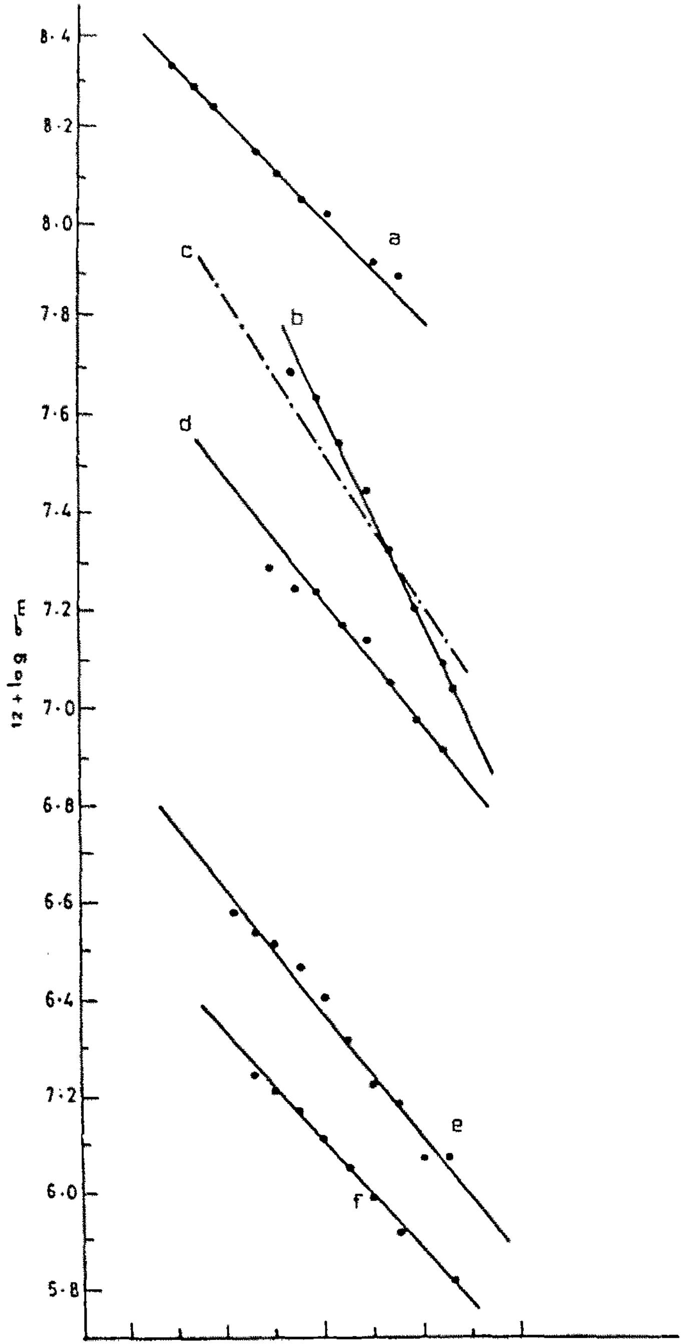

Fig. 4. Electrical conductivity data for: (a) 6-nitrobenzimidazole (L^2) ligand, (b) $Cu_2L_2(OAc)_4$, (c) $CdL_2(OAc)_2$, (d) $ZnL_2(OAc)_2$, (e) $NiL_2(OAc)_2$ and (f) $CoL_4(OAc)_2$.

TABLE 1

Electrical conductivity data for 5-nitrobenzimidazole (L^1), 6-nitrobenzimidazole (L^2) and their metal complexes

Compound	ΔE (eV)	$12+\log \sigma_{25}^{a}$	$-\log \sigma_0$
L^1	0.245	6.42	1.240
$ZnL^1_2Cl_2$	0.286	5.40	1.780
$CdL^1_2Cl_2$	0.268	5.38	2.170
$NiL^1_2Cl_2$	0.212	5.46	2.990
$CuL^1_2Cl_2$	0.137	7.98	1.370
$CoL^1_4Cl_2$	0.129	6.06	3.800
$Cu_2L^1_2(OAc)_4$	0.454	7.31	2.950
$NiL^1_2(OAc)_2$	0.317	6.21	0.269
$ZnL^1_2(OAc)_2$	0.261	7.17	0.344
$CoL^1_4(OAc)_2$	0.230	7.30	0.843
$CdL^1_2(OAc)_2$	0.201	5.86	2.784
$CuL^1_2Br_2$	0.227	5.51	2.744
$CdL^1_2(SO_4)$	0.280	6.27	1.03
L^2	0.294	7.70	0.478
$CuL^2_2Cl_2$	0.289	7.43	0.211
$CoL^2_4Cl_2$	0.272	5.78	1.646
$ZnL^2_2Cl_2$	0.173	7.60	1.474
$NiL^2_2Cl_2$	0.099	6.30	4.686
$CdL^2_2Cl_2$	0.083	7.97	2.622
$Cu_2L^2_2(OAc)_4$	0.580	7.07	4.698
$CdL^2_2(OAc)_2$	0.301	7.14	0.186
$ZnL^2_2(OAc)$	0.259	7.00	0.658
$NiL^2_2(OAc)_2$	0.245	6.04	1.837
$CoL^2_4(OAc)_2$	0.205	5.18	2.722
$CuL^2_2Br_2$	0.251	6.80	0.976
$CdL^2_2(SO_4)$	0.284	5.17	2.069

[a] Electrical conductivity at room temperature (25 ° C).

nature which may arise in some of the complexes as a result of the temperature effects [10,21].

(2) Most of the acetato-complexes have lower electrical conductivity values than the corresponding organic compound, see Table 1. This can be attributed to the bridging nature of the acetato anions between the metal ions.

According to the electrical conductivity values (Table 1) the complexes may be classified as follows.

(a) The electrical conductivity of $[CuL^1_2Cl_2]$ is greater than that of $[CuL^1_2Br_2]$, probably due to distortion from ideal symmetry [1–6]. The lower electronegativity of Br^- compared to that of Cl^- means that Br^- is a softer base than Cl^-, and consequently Br^- has an increased ability to coordinate to the soft acid Cu(II) than has Cl^-. The acetato complexes have intermediate conductivity values between the chloro- and bromo-complexes,

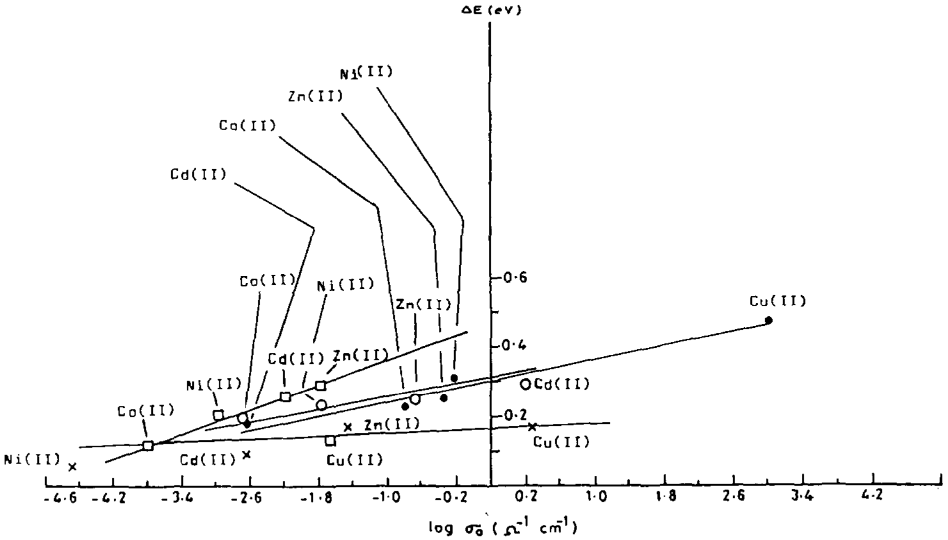

Fig. 5. ΔE vs. log σ_0: ○, 6-nitrobenzimidazole acetate complexes; ●, 5-nitrobenzimidazole acetate complexes; ×, 6-nitrobenzimidazole chloride complexes; □, 5-nitrobenzimidazole chloride complexes.

probably due to their existence in different structures [15]. The same trend was observed in both cobalt(II) and nickel(II) complexes.

(b) In the L^2 complexes, the electrical conductivity values are arranged in the following order: $\mathrm{CdL^2_2Cl_2} > \mathrm{CdL^2_2(OAc)_2} > \mathrm{CdL^2_2(SO_4)_2}$. This is clearly in the reverse order to that of the L^1 complexes. This could be attributed to

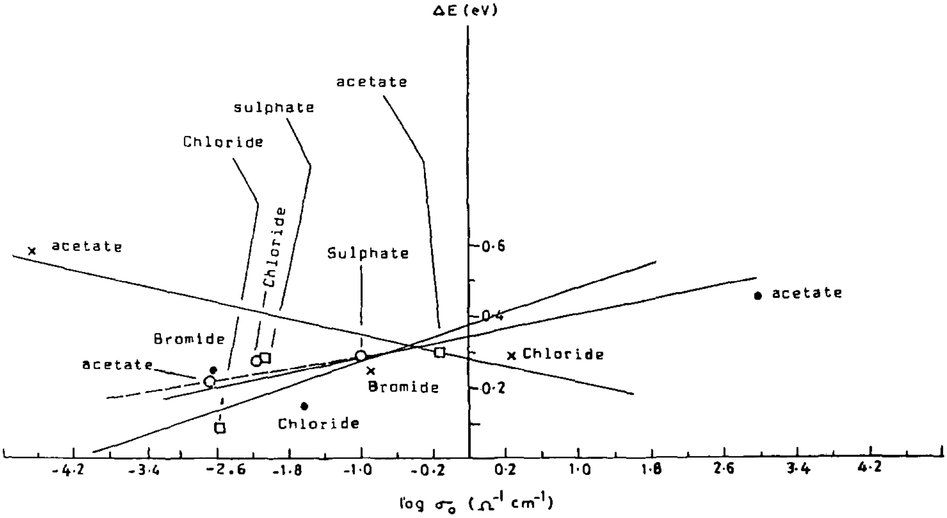

Fig. 6. ΔE vs. log σ_0: ○, cadmium-5-nitrobenzimidazole complexes; ●, copper-5-nitrobenzimidazole complexes; ×, copper-6-nitrobenzimidazole complexes; □, cadmium-6-nitrobenzimidazole complexes.

the steric effect produced by the nitro-group in position 6 in the case of L^2. This is the same behaviour as observed for cobalt(II) and nickel(II) complexes.

(c) Except for copper(II) complexes, the conductivity values were found to increase in the order $OAc^- > Cl^-$ for the L^1 complexes while the opposite behaviour was observed in the L^2 complexes. This may be attributed to an increase in the steric effect when the nitro-group is in position 6 as compared to position 5. Resonance interaction may also be a contributory factor.

REFERENCES

1 M. Muller and D.G. Lindmark, Antimicrob. Agents Chemother., 9 (1976) 696.

2 J.F. Fowler, G.E. Adams and J. Denekamp, Cancer Treat. Rev., 3 (1976) 227.

3 E. Baraniak, H.C. Freeman, J.M. James and C.E. Nockolds, J. Chem. Soc., Ser. A, (1970) 2258.

4 J. Reedijk, Recl. Trav. Chim. Pays-Bas, 90, (1971) 124.

5 D.M.L. Goodgame, M. Goodgame and G.W.R. Canhan, J. Chem. Soc. Set. A, (1971) 1923.

6 K.C. Mohapatra and K.C. Dash, J. Inorg. Nucl. Chem., 39 (1977) 1253.

7 T.M. Salem, M.M. Osman, M.S. Masoud, M.F. El-Shazly and M.M. Abou-Sekkina, Al-Physica, 2 (1979) 43.

8 M.S. Masoud, B.S. Farag, Y.A. Sawan, T.M. Salem and M.M. El-Essawy, J. Non-Crystalline Solids, 55 (1983) 209.

9 M.S. Masoud, E.A. Khalil and M.E. Kassem, Reactivity of Solids, 2 (1986) 269.

10 A. El-Dissouky, A. El-Sonbati and M. Kassem, Thermochim. Acta, 103 (1986) 213.

11 M.S. Masoud, M.E. Kassem, Y. Abd El-Aziz and S. Massoud, Xth Conference on Solid-State Science and Applications, Alexandria 6–9 April, 1987, Mohram Bey Press, p. 46.

12 M.S. Masoud, M.E. Kassem, S. Hedewy and A.R. Yousseff, 1st Regional Symposium of Materials Science (In the Arab States), Alexandria 29–31 December, 1987 Mohram Bey Press.

13 M.S. Masoud, E.M. Soliman and M.E. El-Shabasy, Thermochim. Acta, 125 (1988) 9.

14 M.S. Masoud, A. El-Khatib, M. Kassem and A.R. Yousseff, J. Mater. Sci. Lett., 7 (1988) 1291.

15 W.J. Eilbeck, F. Holmes and A.E. Underhill, J. Chem. Soc. Ser. A, (1967) 757.

16 D.M.L. Goodgame, M. Goodgame, P.J. Hayward and G.W. Rayner-Canham, Inorg. Chem., 7 (1968) 2447.

17 M. Goodgame and L.I.B. Haines, J. Chem. Soc. Ser. A, (1966) 174.

18 V. Cola, P. Souza and J.R. Masaguar, Transition Met. Chem., 11 (1986) 373.

19 K.L. Cheng, Anal. Chem., 27 (1955) 782.

20 G. Schwartzenbach, Complexomeric Titration, Methuen, Vd. I London, 1957.

21 R.D. Dugsibe, Report of Bristol Conference on Defects in Crystalline Solids, The Physical Society, London, 1955, p. 246.