Polymeric charge-transfer complexes: a study by electronic absorption spectroscopy

S. Palaniappan and D. N. Sathyanarayana*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India

The charge-transfer complex formation between an electron donor polymer, namely poly(2-vinyl pyridine) and low molecular weight acceptors namely 7,7',8,8'-tetracyanoquinodimethane and iodine has been investigated by measuring electronic absorption spectra in dichloroethane at 25°C. The formation of charge-transfer complexes of 2-picoline with the same set of acceptors has also been studied as models for comparison. An alternative method has been proposed to determine the molar ratio and equilibrium constant for charge-transfer complex formation by electronic spectroscopy. The equilibrium constant and molar absorptivity for the polymeric complexes are found to be higher than those for the analogous model complexes. The charge-transfer complexes undergo an irreversible reaction to give a final product. The charge-transfer complexes have been studied by electron spin resonance spectra.

(Keywords: charge-transfer complex; electronic absorption spectra; electron spin resonance spectra)

INTRODUCTION

Spectroscopic investigations of charge-transfer complexes in which a polymeric species is a donor and a small molecule is an acceptor have been made[1-9]. In this category, charge transfer complexes of poly(N-vinyl carbazole) have been extensively studied because of their potential applications in electrography. The characteristics of charge-transfer complexes of polymeric donors can be better understood by a comparison of the absorption spectra and the equilibrium constant of polymeric charge-transfer complexes with those of the corresponding low molecular weight models. The relation between the equilibrium constants of the polymeric charge-transfer complexes and those of their low-molecular weight analogues is, however, not clearly understood. This may be due to the inaccuracies in the generally accepted methods for the determination of equilibrium constants of polymeric charge-transfer complexes.

The study of charge-transfer complex formation between poly(vinyl pyridines) with low molecular weight acceptors has special significance because pyridine is the simplest member of an interesting series of electron donor molecules which contain both π and (n)σ electrons for donation. The equilibrium constant of the charge-transfer complexes between poly(vinyl pyridines) with low molecular weight acceptors have not been studied except for a report on the charge-transfer complex of poly(vinyl pyridine) with quinone[10] and no information about the 'polymer effect' is available[11].

The electronic spectra and equilibrium constant for the formation of the charge-transfer complexes between poly(2-vinyl pyridine) (PVP) and low molecular weight acceptors namely iodine (I_2) and 7,7',8,8'-tetracyanoquinodimethane (TCNQ) have been studied. The results are compared with those obtained for charge-transfer complex formation involving the analogous low molecular weight donor namely 2-picoline (PIC) with the same set of acceptors. A method for the determination of the equilibrium constant for charge-transfer complex formation in solution is proposed and employed in the present study. The charge-transfer complexes have also been studied by electron spin resonance spectra.

EXPERIMENTAL

Materials

Poly(2-vinyl pyridine) (Aldrich) was dissolved in AR grade benzene and reprecipitated from the filtrate using excess of AR grade n-hexane. The procedure was repeated three times. The product was dissolved in chloroform and filtered through a G-3 crucible. The solvent was evaporated under reduced pressure.

2-Picoline (BDH) was kept over KOH pellets overnight and distilled under vacuum. Only the middle fraction was collected.

7,7',8,8'-tetracyanoquinodimethane (Aldrich) was used; m.p. 296°C. Iodine was purified by sublimation under vacuum.

Dichloroethane (BDH) was treated twice with 10% sulphuric acid, then twice with 10% NaOH and washed repeatedly with water. It was dried over anhydrous calcium chloride and distilled.

Measurements

Electronic absorption spectra. Absorption spectra measurements were obtained in dichloroethane at 25°C using an Hitachi U-3400 spectrophotometer. The electronic spectra of the CT complexes were recorded in the range 200–1200 nm using a pair of matched 3 ml stoppered silica cells of 10 mm path length.

Two sets of measurements were made. For the first set a standard solution of the donor in dichloroethane was made by dissolving a known amount of the donor in

---

10 ml of the solvent in a volumetric flask. A series of solutions containing 1 ml of the donor and 2 ml of the acceptor (different concentrations) with a final volume of 3 ml were prepared. Here the concentration of the donor is kept greater than that of the acceptor. For the second set a standard solution of the acceptor in dichloroethane was made by dissolving a known amount of the acceptor in 10 ml of the solvent in a volumetric flask. A series of 1 ml solutions of the acceptor (fixed concentration) and 2 ml of the donor (different concentrations), making a total volume of 3 ml, were prepared. Again the concentration of the donor was kept greater than that of the acceptor.

The solutions were repeatedly degassed using pure and dry N_2. The whole operation was carried out in dim light. The absorption spectra of these solutions were recorded immediately after mixing and at different time intervals using dichloroethane as the reference.

Electron spin resonance spectra. The e.s.r. spectra of the complexes were obtained on a Varian E-109 ESR spectrometer operating in the X-band. The solutions of each constituent in dichloroethane at room temperature were mixed. The spectra were recorded in solution state. The g values and line widths were estimated by taking charred dextrose as the standard.

RESULTS AND DISCUSSION

Solutions containing the interacting donor (D) and acceptor (A) species show not only the absorption bands of D and A, but most often also exhibit a new band or bands which are assignable to charge-transfer transitions of the complex as a whole. The intensity of this band could be used as a measure of the concentration of the complex in a given solution. Another general feature of charge-transfer interaction is the possibility of complete electron transfer from donor to acceptor with the formation of free radicals. The variation in the absorption band intensity of one of the components as the concentration of the other component is increased may also be used to estimate the composition of the charge-transfer complex (D:A) and equilibrium constant (K). Charge-transfer complex may further undergo an irreversible chemical reaction to give a final product.

The formation of charge-transfer complex was studied spectrophotometrically in dichloroethane at 25°C. We focused our attention chiefly on the charge-transfer complexes and no efforts were made towards product analysis.

Calculation of equilibrium constant

The interaction between an electron donor (D) and an electron acceptor (A) resulting in the formation of a donor-acceptor complex (DA) can be represented as

$$mD + nA \rightleftharpoons D_m A_n$$
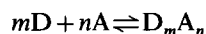
Let us consider the electronic absorption spectra of a series of solutions containing a fixed amount of the donor and varying amounts of the acceptor, keeping the concentration of the donor much greater than that of the acceptor. That is,

$$D + nA \rightleftharpoons DA_n$$

If d is the initial concentration of D, and a is the original concentration of A, and the concentration of the complex

(DA) formed is x, then the equilibrium constant for the reaction in concentration units is given by

$$K = x/(d-x)(a-nx)^n \qquad (1)$$

$d \gg a$ and $x < a$

$$K = x/d(a-nx)^n \qquad (2)$$

If the complex obeys Beer's law at a given wavelength, the total absorbance per cm (OD) is given by

$$x = OD/\varepsilon \qquad (3)$$

and

$$x = az/n \qquad (4)$$

where ε denotes the molar extinction coefficient of the charge-transfer complex and z the percentage conversion of a.

On substituting equation (4) in equation (2), we get

$$K = az/dna^n(1-z)^n \qquad (5)$$

1:1 complex

Equation (2) leads to

$$K = x/d(a-x) \qquad (6)$$

Substituting the value of x from equation (3) to equation (6), we obtain,

$$K = OD/d(a\varepsilon - OD) \qquad (7)$$

For solutions of different acceptor concentrations (as in the present case), we have

$$OD_1/d(a_1\varepsilon - OD_1) = OD_2/d(a_2\varepsilon - OD_2) = \cdots$$

that is,

$$OD_1/OD_2 = a_1\varepsilon - OD_1/a_2\varepsilon - OD_2$$

On simplification we obtain,

$$OD_1/a_1 = OD_2/a_2$$

That is,

$$OD/a = \text{constant} \qquad (8)$$

From the percentage conversion of the lower concentration component, the value of K can be calculated using the equations (3), (4) and (7).

1:n complex

Substitution of the value of x from equation (3) in equation (2) leads to

$$K = OD\varepsilon^n/d\varepsilon(a\varepsilon - nOD)^n \qquad (9)$$

For solutions of different acceptor concentrations, equation (9) gives

$$OD_1/(a_1\varepsilon - nOD_1)^n = OD_2/(a_2\varepsilon - nOD_2)^n = \cdots$$

On simplification and rearrangement, we obtain,

$$\varepsilon = \frac{n[(OD_1^{1/n}OD_2) - (OD_1 OD_2^{1/n})]}{(OD_1^{1/n}a_2) - (OD_2^{1/n}a_1)} \qquad (10)$$

For various assumed values of n (ranging say from 0.1 to 5.0 in steps of 0.1), the ε values are calculated. For a particular value of n, the calculated ε values will become the same and that value of n represents the molar ratio. Before and after this value of n there will be variation in the calculated ε values. Using this value of n and the corresponding ε value, K is calculated from equation (9).

PVP–I_2 and PVP–TCNQ systems

The absorption maxima of the donor PVP and the acceptors (I_2, TCNQ) and their charge-transfer complexes are given in *Table 1*. In all our experiments we have taken higher concentration of the donors and lower concentration of the acceptors because of the poor solubility of TCNQ. The molar ratio, molar absorptivities and equilibrium constant for the charge-transfer complexes are given in *Table 2*.

A yellow colour ($\lambda_{max} = 365.5\,nm$) is produced immediately after PVP and I_2 are mixed in dichloroethane and the optical density of this solution increases with time (*Figure 1*). This colour is ascribed to the formation of a charge-transfer complex between the reactants. The absorption spectra of the iodine and PVP–I_2 charge-transfer complex are shown in *Figure 2*. The optical density (at $\lambda_{max} = 365.5\,nm$) decreases gradually and the absorption maximum shifts to the ultraviolet in 48 h. The spectrum of the final product, a colourless solution, exhibits absorption peaks at 257.2, 262.4 and 268.7 nm (*Figure 2*). E.s.r. spectra were measured immediately after

Table 1 Absorption maxima of the donors, acceptors and their complexes in dichloroethane
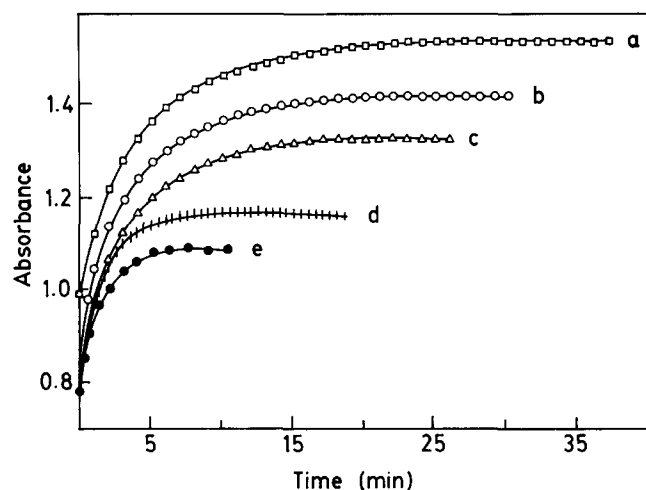
| Compound	λ_{max} (nm)			
	λ_1	λ_2	λ_3	λ_4
PVP	257.5	263.0	269.5	
PIC	257.0	263.5	271.0	
I_2	503.0			
TCNQ[d]	402.0			
PVP–I_2[a,d]	365.5			
PVP–I_2[c]	257.0	262.5	269.0	
PVP–TCNQ[a,d]	684.0	751.0	768.5	851.5
PVP–TCNQ[b,d]	485.0	631.0	664.0	
PVP–TCNQ[c,d]	484.5			
PIC–I_2[a,d]	366.0			
PIC–TCNQ[a,d]	684.5	750.5	768.0	851.5

[a] Charge-transfer complex
[b] Intermediate
[c] Product
[d] Spectra were recorded between 350–1200 nm

Figure 1 Variation of absorbance with time for the PVP–I_2 system ($\lambda_{max} = 365.5\,nm$ in dichloroethane) for different concentrations of iodine. Curve (a) $1.61 \times 10^{-4}\,M$; curve (b) $1.51 \times 10^{-4}\,M$; curve (c) $1.42 \times 10^{-4}\,M$; curve (d) $1.26 \times 10^{-4}\,M$ and curve (e) $1.18 \times 10^{-4}\,M$ with the concentration of PVP kept at $3.37 \times 10^{-3}\,M$
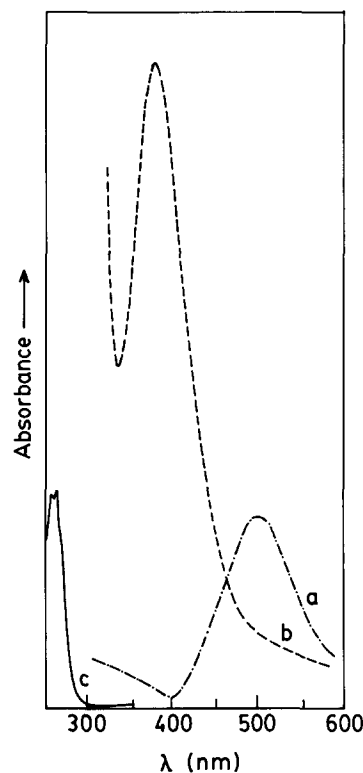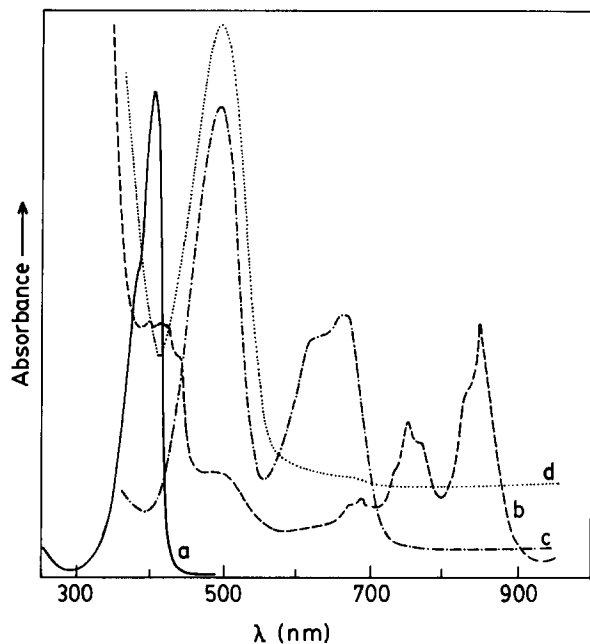
Figure 2 Absorption spectra of iodine (curve a); charge-transfer complex of PVP–I_2 (curve b) and its final product in dichloroethane (curve c)

the solutions of the reactants (PVP and I_2) in dichloroethane were mixed. The e.s.r. signals were not observed for this system. These results suggest that the reaction between PVP and I_2 involve two steps: first the formation of charge-transfer complex occurring without the formation of free radicals, and then the final product.

The position of the charge-transfer band is dependent on the concentration of the donor. However, we did not observe any variation of the absorption maximum with (the limited) variation of iodine concentration.

Several new bands are found (*Table 1*) immediately after PVP and TCNQ are mixed in dichloroethane. The multiplicity of bands may arise from electron donation from more than one energy level in the donor to the lowest unoccupied molecular orbital of the acceptor or from the highest occupied orbital of the donor to the different energy levels in the acceptor, or from a combination of these two possibilities. Frequently it is due to electronic transitions from more than one level in the donor to the acceptor. The new bands are easily ascribed to a charge-transfer complex formation between the reactants (*Figure 3*). The absorption band intensity of the charge-transfer complex decreases gradually. This may be due to the charge-transfer complex possibly producing an intermediate which shows absorption bands at 664.0, 630.7 and 484.8 nm (*Figure 3*). Finally these bands disappear and the spectrum of the final product, which has a golden yellow colour, has a peak at 484.4 nm (*Figure 3*). E.s.r. spectra were measured immediately after the solutions of the reactants (PVP and TCNQ) in dichloroethane were mixed. The g values and line widths of the charge-transfer complex are 2.0080 and 4.6 Gauss respectively. The signal intensity (spin concentration) increases rapidly attaining a maximum (and this corresponds to the formation of the charge-transfer

Figure 3 Absorption spectra of TCNQ (curve a) and PVP–TCNQ charge-transfer complex (curve b) intermediate (curve c) and the final product (curve d) in dichloroethane

complexes which was confirmed by measuring the electronic spectra) and then decreasing gradually. Finally the paramagnetism of the solution vanishes (and this corresponds to the formation of the product). These results suggest that the reaction between PVP and TCNQ involves three steps: formation of charge-transfer complexes occur with the formation of free radicals, an intermediate and finally the product.

PIC–I_2 and PIC–TCNQ systems

The absorption maxima of PIC and its charge-transfer complexes are given in *Table 1*. The molar ratio, molar absorptivity and equilibrium constant for the charge-transfer complexes are included in *Table 2*. The *g* values and line widths are 2.0070 and 3.7 Gauss respectively for the PIC–TCNQ system and e.s.r. signals were not observed for the PIC–I_2 system.

The maximum optical density (OD_∞) corresponding to the formation of charge-transfer complexes varies with different concentration of the acceptors (when the concentration of the donor is kept much greater than that of the acceptors) and this is plotted in *Figure 4*. Linear plots were found for the polymer charge–transfer complexes and this indicates the formation of a 1:1 complex. When good straight lines are not obtained, it indicates the formation of a 1:n complex as observed for the low molecular weight charge-transfer complexes.

The same spectral behaviour was found for the formation of polymeric as well as low molecular weight charge-transfer complexes except that the values of the equilibrium constants and molar absorptivities for the polymer charge-transfer complexes are much larger than those found for the corresponding model complexes (*Table 2*) while the times required for the formation of the product from polymer charge-transfer complexes are lower than those from the model complexes (which take several days to form the product, and hence product analyses are difficult). If we assume complexing to occur perpendicular to the polymer backbone (where the

acceptor is not sandwiched between the donors) there is no reason to expect stronger complexing for the polymer than for the model. The small inductive effect of the methylene group of PVP makes it a slightly better donor; therefore, it may form a slightly stronger complex. However, the differences seen here are too large to account for this. When we compare inductive effects of methyl *versus* methylene in the case of PIC and PVP, they should be nearly the same. Therefore, inductive effects cannot explain the stronger complexing of the polymer. A reasonable explanation seems to be that the complexing is enhanced in the direction to the polymer backbone. The spatial restrictions on the polymer donor, provides room for an acceptor to sandwich between the donors. Proper geometry is, it appears, then responsible for the stronger complexing and higher equilibrium constant in the polymer. The charge-transfer complexes formed between poly(2-vinyl pyridine) with low molecular weight acceptors do not show bathochromic shift in the charge-transfer absorption maximum when compared to the model complexes. Thus 'polymer effect' was not observed in the case of charge-transfer complexes of the vinyl polymer with large pendent π-electron systems. Product analyses of the polymeric complexes are under progress.

Comparison between the present method and previous methods

It was found that when the concentration of the donor is kept much greater than that of the acceptor the absorption spectra of a series of solutions containing a

Table 2 Molar ratio (n), molar absorptivity (ε) and equilibrium constant (K) of the charge-transfer complexes

Complex	n	ε (l mol^{-1} cm^{-1})	K (l mol^{-1})
PVP–I_2	1:1	13 850	602.9
PVP–TCNQ	1:1	21 180	269.4
PIC–I_2	1:0.5	3620	2.7[a]
PIC–TCNQ	1:0.5	1470	1.8[a]

[a] (l mol^{-1})$^{0.5}$
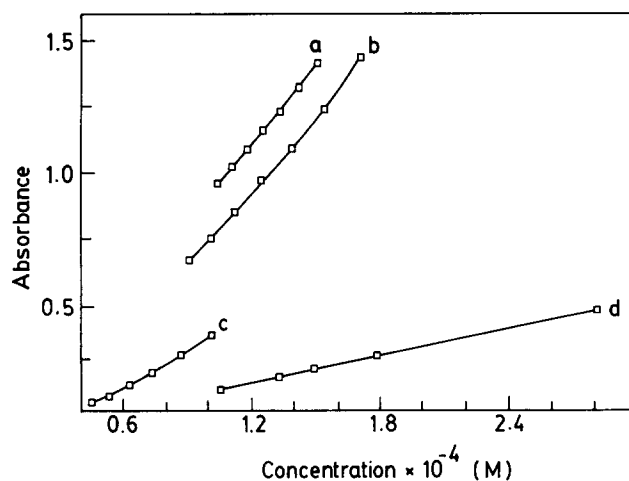
Figure 4 Variation of absorbance with concentration of acceptors; curve a, PVP–I_2 ($\lambda_{max}=365.5$ nm); curve b, PIC–I_2 ($\lambda_{max}=366.0$ nm); curve c, PIC–TCNQ ($\lambda_{max}=851.5$ nm) and curve d, PVP–TCNQ ($\lambda_{max}=851.5$ nm) systems in dichloroethane

fixed amount of the acceptor and varying amounts of the donor show constant absorption maxima (OD_∞). This is because the donor concentration is kept much greater than that of the acceptor. When the ratio of the concentration of the donor to the acceptor is decreased, it takes a longer time to reach the equilibrium charge-transfer complex formation (4 or 5 days), thus rendering it very difficult to monitor the reaction. It is therefore not possible to obtain the molar ratio (n) and the equilibrium constant (K) for the unstable charge transfer complexes using the available methods[12-18]. Rose and Drago[17], and Ketelaar[18] have proposed a new equation for the determination of equilibrium constant for the formation of charge-transfer complexes. From a practical point of view, an application of the expression given by Rose and Drago, and Ketelaar, would require many calculations to be made (e.g. molar absorptivity of the donor and acceptor) before the equilibrium constant could be obtained.

In the calculation of equilibrium constant for the polymeric charge-transfer complexes, molar absorptivity of the polymer cannot be calculated. Therefore, these methods cannot be utilized. An alternative method is therefore proposed to determine the equilibrium constant. The advantage of the present method is that the molar ratio and equilibrium constants can be directly evaluated. Any desired proportion of the donor and acceptor concentration can be employed and the molar absorptivities of the donor and acceptor are not needed. The absorption intensity need not be extrapolated to the time of mixing[19] and also there is no need for the absorption spectral measurements immediately after mixing the reactants[20] or after keeping the solutions to a particular length of time[10]. However, the present method is only applicable to systems when the optical absorption is due to the charge-transfer complex (AD) and when one of the components is in large excess.

CONCLUSION

The reaction of poly(2-vinyl pyridine) with TCNQ in dichloroethane occurs in three steps, involving the formation of a charge-transfer complex, an intermediate and then the final product. The reaction of poly(2-vinyl pyridine) with iodine occurs likewise, but in two steps, involving the formation of charge-transfer complex and then the final product. The same situation was found for the interaction between picoline with TCNQ and iodine. Formation of the charge-transfer complexes is very fast and this is followed by a very slow irreversible reaction to the product. The time required for attaining the product is very long for the complexes of low molecular weight compared to the time needed for the polymeric charge-transfer complexes. Polymer effect was not observed in the present study. The equilibrium constant for the polymeric charge-transfer complexes is larger than that for the low molecular weight donor complexes and the polymeric charge-transfer complexes are more stable than the complexes of their low molecular weight analogues. Proper geometry is a factor responsible for the stronger complex formation and higher equilibrium constant in the polymer.

REFERENCES

1   Gang, E. T. *Eur. Polym. J.* 1985, **21**, 919
2   Kogi, A., Susumu, H., Yoshihiro, I. and Saburo, S. *Makromol. Chem.* 1985, **186**, 1505
3   Iwatsuki, S. and Arai, K. *Makromol. Chem.* 1977, **178**, 2307
4   Tazuke, S., Sato, K., Banba, F. and Matsuyama, Y. *J. Polym. Sci., Polym. Lett. Edn.* 1976, **14**, 653
5   Matsuyama, Y. and Tazuke, T. *Makromol. Chem.* 1975, **176**, 1657
6   Iwatsuki, S. and Inukai, K. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 1437
7   Boudevska, H. *Makromol. Chem.* 1971, **143**, 11
8   Klopffer, W., Tacheci, H. and Willicks, W. *Makromol. Chem.* 1969, **126**, 147
9   Kryzewski, M. *J. Polym. Sci. B* 1966, **4**, 2281
10   Sugiyama, H. and Kamogawa, H. *J. Polym. Sci. A-1* 1966, **4**, 2281
11   Iwatsuki, S. and Arai, K. *J. Polym. Sci., Polym. Chem. Edn.* 1972, **10**, 3329
12   Benesi, H. A. and Hildebrand, J. H. *J. Am. Chem. Soc.* 1949, **71**, 2703
13   Scott, R. C. *Rec. Trav. Chim.* 1956, **75**, 785
14   Nagakuru, S. *J. Am. Chem. Soc.* 1958, **80**, 520
15   Nash, C. P. *J. Phys. Chem.* 1960, **64**, 950
16   Tamres, M. *J. Phys. Chem.* 1961, **65**, 654
17   Rose, N. J. and Drago, R. S. *J. Am. Chem. Soc.* 1959, **81**, 6138
18   Ketelaar, J. A. A., Stolpe, C. V. and Gersmann, H. R. *Rec. Trav. Chim.* 1952, **70**, 499
19   Rappoport, Z. *J. Chem. Soc.* 1963, 4498
20   Srivastava, R. D. and Prasad, G. P. *Spectrochim. Acta* 1966, **22**, 1869