Substitution of Acetonitrile co-ordinated to Iron(II) by Trimethyl Phosphite: A Kinetic Study of the Formation and Disappearance of $[Fe(NCMe)_4\{P(OMe)_3\}_2]^{2+}$ †

By **James H. Cameron, A. Graham Lappin,*** and **John M. Winfield,*** Department of Chemistry, University of Glasgow, Glasgow G12 8QQ
Alexander McAuley, Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada

The red soluble species formed by mixing solutions of $[Fe(NCMe)_6]^{2+}$ and trimethyl phosphite in acetonitrile at room temperature has been identified as low-spin $[Fe(NCMe)_4\{P(OMe)_3\}_2]^{2+}$ from a stopped-flow spectrophotometric kinetic study. An interchange mechanism, occurring *via* an outer-sphere complex, is proposed for its formation, the relatively slow interchange step, $k_i = 1.03 \pm 0.10$ s^{-1} at 297 ± 0.1 K, being a consequence of steric control by $P(OMe)_3$. Subsequent reactions which involve the formation of $[Fe(NCMe)_{6-n}\{P(OMe)_3\}_n]^{2+}$ (n = 3 or 4) are far slower. Formation of the trisubstituted cation is first order in $[P(OMe)_3]$.

THE study of iron–trimethyl phosphite complexes has received much attention in recent years, and a number of complexes containing Fe^0 or Fe^{II} are known.[1] Recently, we have reported on the reaction between $P(OMe)_3$ and the hexakis(acetonitrile)iron(II) cation in acetonitrile solution which involves the stepwise replacement of co-ordinated MeCN by $P(OMe)_3$. The final product obtained at room temperature is $[Fe(NCMe)\{P(OMe)_3\}_5][PF_6]_2$.[2] Although four intermediate cations $[Fe(NCMe)_{6-n}\{P(OMe)_3\}_n]^{2+}$, $n = 3$ (*fac* and *mer*), $n = 4$ (*cis* and *trans*), can be identified positively by ^{31}P-$\{^1H\}$ n.m.r. spectroscopy, and a tentative assignment made for $[Fe(NCMe)_4\{P(OMe)_3\}_2]^{2+}$, this technique is of little use for studying the initial steps in the reaction sequence. A similar situation has been found for the related reactions of $P(OMe)_3$ with $[Fe(thf)_2X_2]$ (thf= tetrahydrofuran; X = Cl, Br, or I).[1d]

In order to clarify the initial part of the reaction sequence and, in particular, to identify the step at which the high-spin–low-spin crossover occurs, we have undertaken a kinetic study by electronic spectroscopy and the results of this are now reported.

RESULTS AND DISCUSSION

Stopped-flow Studies.—Addition of an excess of $P(OMe)_3$ in MeCN to a colourless solution of $[Fe(NCMe)_6][PF_6]_2$ in MeCN at room temperature results in the formation of a red soluble species. Its formation is too rapid to be followed by electronic spectroscopy using conventional methods, but it is conveniently within the stopped-flow range. The electronic spectrum of the species, obtained by point-by-point determination over the range 17 000—33 000 cm^{-1}, $Fe^{II} : P(OMe)_3 = 1 : 100$, consists of two bands with maxima at 23 000 and 29 000 cm^{-1}, $\varepsilon = 320$ and 270 dm^3 mol^{-1} cm^{-1} respectively. This spectrum is essentially identical to the 'initial' spectrum of the reaction mixture obtained by conventional means,[2] and is independent of the ratio $Fe^{II} : P(OMe)_3$ over the range 1 : 50—1 : 500. By analogy with the spectra of $[Fe(NCMe)\{P(OMe)_3\}_5]^{2+}$ (ref. 2) and $[Co\{P(OMe)_3\}_6]^{3+}$ (ref. 3) the red species has a ground state derived from a t_{2g}^6 configuration.

Comparison with ^{31}P-$\{^1H\}$ n.m.r. spectra obtained from the initial stages of reaction [2] indicate that the red species can be assigned either as $[Fe(NCMe)_5\{P(OMe)_3\}]^{2+}$ or $[Fe(NCMe)_4\{P(OMe)_3\}_2]^{2+}$. However, spectrophotometric determination of the overall formation constant of the red species indicates that the latter assignment is to be preferred. Solutions in which the ratio $Fe^{II} : P(OMe)_3$ is 2 : 1, 1 : 1, or 1 : 2 are yellow, but their electronic spectra contain the two bands described above in addition to a broad, asymmetric band with a maximum at 11 300 cm^{-1}, typical of high-spin Fe^{II}. The assumption of a 1 : 1 complex does not produce consistent values for the formation constant, but consistent values are obtained if a 1 : 2 complex is assumed, the derived value being $(1.0 \pm 0.2) \times 10^3$ dm^6 mol^{-2}.

We conclude that the formation of $[Fe(NCMe)_5\{P(OMe)_3\}]^{2+}$ is very rapid and that this species is not detectable using our stopped-flow equipment. This implies that the transition from high- to low-spin Fe^{II} occurs with the formation of $[Fe(NCMe)_4\{P(OMe)_3\}_2]^{2+}$. The ^{31}P-$\{^1H\}$ n.m.r. signal assigned to this species [2] suggests that it has a *cis* configuration, but is not definitive.

In the presence of a large excess of $P(OMe)_3$, the rate of formation of the red species, $[Fe(NCMe)_4\{P(OMe)_3\}_2]^{2+}$, is pseudo-first order in $[Fe^{II}]$. The pseudo-first-order rate constants, $k_{obs.}$, at 297 ± 0.1 K show a limiting dependence on the concentration of $P(OMe)_3$, Figure 1, which can be accounted for by an expression of the form (1). Constants a and b were determined by least-squares analysis of the reciprocal of equation (1) to be 4.17 ± 0.20 dm^3 mol^{-1} s^{-1} and 4.04 ± 0.48 dm^3 mol^{-1} respectively.

$$k_{obs.} = a[P(OMe)_3]/\{1 + b[P(OMe)_3]\} \qquad (1)$$

Both dissociative and interchange mechanisms can give rise to rate laws of this type,[4] and it should be noted that the limiting rate behaviour observed could also result from a medium effect, since the composition of the solvent changes over the range examined. However, such a marked effect, and change in order, is considered unlikely.

The limiting rate constant a/b, 1.03 ± 0.08 s^{-1}, is very

---

† Tetrakis(acetonitrile)bis(trimethyl phosphite)iron(II).

much smaller than the rate constant for solvent exchange at $[Fe(NCMe)_6]^{2+}$. This has been determined to be 5.5×10^5 s^{-1} by ^{14}N n.m.r. spectroscopy.[5] High-pressure n.m.r. studies involving dipositive 3*d* metal cations in methanol indicate dissociative-interchange behaviour for Co^{II} and Ni^{II}, associative-interchange behaviour for Mn^{II}, and an intermediate situation for Fe^{II}.[6] Analogous behaviour has been suggested for cobalt(II) and nickel(II) cations in MeCN.[7] A pure dissociative mechanism for the reaction between $[Fe(NCMe)_5\{P(OMe)_3\}]^{2+}$ and $P(OMe)_3$ does not seem likely, and we propose that the reaction proceeds *via* the formation of an outer-sphere complex followed by an interchange step, equation (2); N = MeCN, P = $P(OMe)_3$.

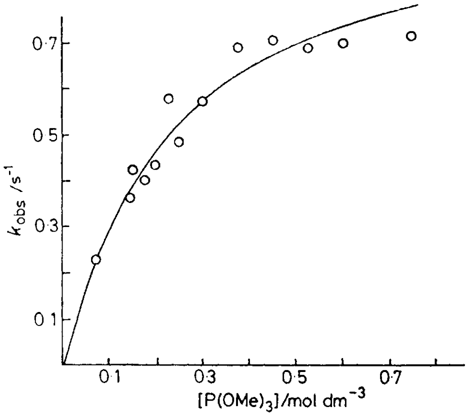

FIGURE 1 Plot of $k_{obs.}$ against $[P(OMe)_3]$ for the formation of the red species

$$[FeN_5P]^{2+} + P \overset{K_{o.s.}}{\rightleftharpoons} \{FeN_5P \cdots P\}^{2+}$$

$$\{FeN_5P \cdots P\}^{2+} \xrightarrow{k_i} [FeN_4P_2]^{2+} + N \quad (2)$$

The values of the interchange rate constant, k_i, and the outer-sphere association constant, $K_{o.s.}$, determined from equation (1) are 1.03 ± 0.10 s^{-1} and 4.04 ± 0.50 dm^3 mol^{-1} respectively. The value of $K_{o.s.}$ is somewhat greater than those normally found for outer-sphere association of metal(II) cations by uncharged ligands in aqueous solution,[8] but the difference is most likely to be a reflection of the different solvent properties of MeCN.[9]

The slow interchange step observed in the present reaction is very unusual for high-spin Fe^{II}, and we believe that the most satisfactory rationalisation for this at the present time is in terms of steric control by the entering $P(OMe)_3$ ligand. In recent years it has become apparent that steric requirements of substituted phosphine ligands are at least as important as electronic effects. In some cases steric factors may be dominant, and the cone angle at phosphorus has been used to explain experimentally observed phenomena.[10] The ligand $P(OMe)_3$ is bulky with a cone angle of 107 ± 2°, and we suggest that this steric requirement dominates its behaviour as a ligand towards Fe^{II}.

Neither $P(OPh)_3$ nor PF_3 appears to react with $[Fe(NCMe)_6]^{2+}$ under comparable conditions, but this may be for both electronic and steric reasons.[2] In contrast, the reaction between $[Fe(NCMe)_6]^{2+}$ and 2,2′-bipyridyl in MeCN is complete within the deadtime of the stopped-flow equipment (50 ms). Bipyridyl is expected to be a better ligand than $P(OMe)_3$ towards Fe^{II} on electronic grounds, and it has some flexibility when entering the first co-ordination sphere.

Subsequent Complexation Steps.—The subsequent steps in the reaction between $[Fe(NCMe)_6]^{2+}$ and $P(OMe)_3$ are much slower than the formation of $[Fe(NCMe)_4\{P(OMe)_3\}_2]^{2+}$ and can be followed by conventional spectrophotometry. A set of spectra typical of those obtained is shown in Figure 2. Shifts in the positions of the isosbestic points, Table 1, indicate a number of consecutive processes, and the simplest analysis involves three such processes. Identification of the species involved, including isomers when present, is aided by the ^{31}P-$\{^1H\}$ n.m.r

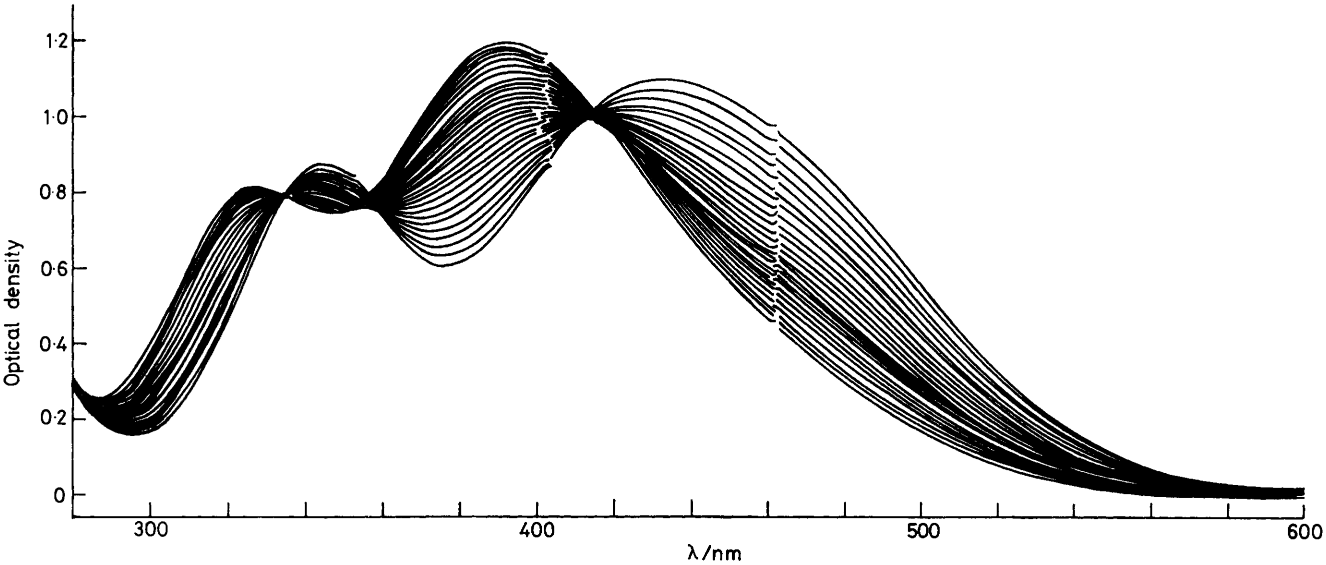

FIGURE 2 Electronic spectra of $[Fe(NCMe)_6]^{2+} + P(OMe)_3$ in MeCN. $[Fe^{II}] = 3.4 \times 10^{-3}$ mol dm^{-3}, $[P(OMe)_3] = 0.457$ mol dm^{-3}

TABLE 1

Variation with time of the electronic spectra of a $[Fe(NCMe)_6]^{2+}$–$P(OMe)_3$ mixture in MeCN

$\nu_{max.}/cm^{-1}$ *	Isosbestic points/cm^{-1}
23 000, 29 000 (320) (270)	
← Step 1 →	24 750 27 800 29 850
24 100, 29 400 (290) (250)	
← Step 2 →	24 200 28 100 29 850
25 650, 30 700 (350) (240)	

* Values of $\epsilon/dm^3\ mol^{-1}\ cm^{-1}$ are given in parentheses.

results for this system.[2] Although the n.m.r. study used more concentrated solutions and was not performed under pseudo-first-order conditions, the differences are sufficiently small for extrapolations to be made.

The first two steps occur at comparable rates with half-lives of the order of minutes, while the third step is very slow with a half-life of the order of days. The latter step was not studied extensively and no data are included in Table 1, but the final spectrum obtained after several days is identical to that of the $[Fe(NCMe)\{P(OMe)_3\}_5]^{2+}$ cation.[2]

Absorbance changes for the first and second steps are not readily separable. However the initial rate of decay of the red species, $[Fe(NCMe)_4\{P(OMe)_3\}_2]^{2+}$, shows a first-order dependence on the concentration of $P(OMe)_3$, Figure 3, suggesting that the formation of $[Fe(NCMe)_3\{P(OMe)_3\}_3]^{2+}$ is rate determining in the first step, equation (3); N = MeCN, P = $P(OMe)_3$. The ^{31}P-$\{^1H\}$ data [2] indicate that *fac*-$[Fe(NCMe)_3\{P(OMe)_3\}_3]^{2+}$ is the kinetically favoured isomer, and this would be the expected product from *cis*-$[Fe(NCMe)_4\{P(OMe)_3\}_2]^{2+}$ if no rearrangement process occurs during the substitution reaction. The *mer* isomer is not observed initially,[2] and its appearance during the later stages of reaction is presumed to be due to a *fac* ⟶ *mer* rearrangement.

$$[FeN_4P_2]^{2+} + P \longrightarrow fac\text{-}[FeN_3P_3]^{2+} + N \qquad (3)$$

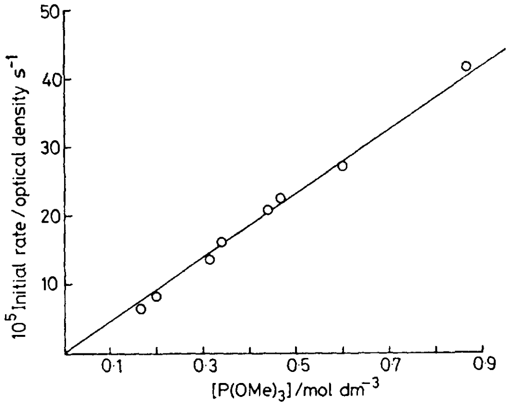

FIGURE 3 Plot of initial rate against $[P(OMe)_3]$

Absolute rate constants, k_1, for the first step (Table 2) were evaluated from absorbance measurements at 24 200 cm^{-1} where there is an isosbestic point for the second reaction. Under pseudo-first-order conditions with a large excess (⩾50-fold) of $P(OMe)_3$ an exponential absorbance change is found for greater than two half-lives. A plot of k_2 against $P(OMe)_3$ concentration is linear and confirms the initial rate prediction. The second-order rate constant at 297 ± 0.1 K is $(1.4 \pm 0.2) \times 10^{-3}\ dm^3\ mol^{-1}\ s^{-1}$.

TABLE 2

Rate constants, k_1, for the reaction $[FeN_4P_2]^{2+} + P \longrightarrow [FeN_3P_3]^{2+} + N$, where N = MeCN and P = $P(OMe)_3$

10^4k_1 */s^{-1}	$[P(OMe)_3]/mol\ dm^{-3}$
2.22	0.163
2.65	0.193
4.67	0.307
4.75	0.334
6.42	0.434
7.47	0.457
8.25	0.591
11.3	0.862

* Error ±10%.

A consecutive-reaction treatment [11] was employed in an attempt to evaluate rate constants for the second step using data at 21 300 cm^{-1} where there is a large absorbance change for both reactions. The absorption coefficients at 21 300 cm^{-1} for the species involved (Table 3) were estimated from the initial-rate data and total-absorption measurements. Unsatisfactory fits to the experimental data were obtained using these parameters, suggesting that the reaction is more complex than allowed for in the kinetic treatment. Logically this step involves the formation of $[Fe(NCMe)_2\{P(OMe)_3\}_4]^{2+}$ from $[Fe(NCMe)_3\{P(OMe)_3\}_3]^{2+}$ and the discrepancies observed may originate from interference of the third step, producing $[Fe(NCMe)\{P(OMe)_3\}_5]^{2+}$, from the *fac* ⟶ *mer* rearrangement of $[Fe(NCMe)_3\{P(OMe)_3\}_3]^{2+}$, or may reflect computational difficulties.

TABLE 3

Estimated absorption coefficients at 21 300 cm^{-1}

Species *	$\epsilon/dm^3\ mol^{-1}\ cm^{-1}$
$[FeN_4P_2]^{2+}$	290
$[FeN_3P_3]^{2+}$	195
$[FeN_2P_4]^{2+}$	*ca.* 100

* N = MeCN, P = $P(OMe)_3$.

Both associative and dissociative mechanisms have been suggested for substitution reactions of low-spin Fe^{II} in water, depending on the nature of the ligands involved.[12] The uncomplicated rate laws and lack of comparable data make mechanistic assignments difficult for these reactions, however it is clear that replacement of MeCN by the sterically demanding $P(OMe)_3$ ligand becomes progressively more difficult.

EXPERIMENTAL

The procedure for the preparation of hexakis(acetonitrile)iron(II) hexafluorophosphate and for the purification of trimethyl phosphite and acetonitrile have been described previously.[2] Kinetic measurements were carried out either using stopped-flow equipment,[13] which was modified to enable solutions to be stored and manipulated under dry N_2, or a Beckman 5270 spectrometer. In each case reactions were studied at 297 ± 0.1 K.

The stopped-flow study employed MeCN solutions of $[Fe(NCMe)_6]^{2+}$, 3.0×10^{-3} mol dm^{-3}, and $P(OMe)_3$, 0.15—1.5 mol dm^{-3}, and was made under pseudo-first-order conditions. Solutions (25 cm^3) were prepared in an argon atmosphere glove-box (Lintott Engineering Co.; <10 p.p.m. H_2O) and were transferred to flasks fitted with glass, polytetrafluoroethylene stopcocks. The flasks were degassed and flamed out *in vacuo* before use. The major source of error in the experiments was loss of volatile $P(OMe)_3$ during transfer of solutions. This was particularly serious for dilute solutions, and transfers were made as quickly as possible. Prior to each experimental run, the stopped-flow equipment was flushed with N_2 for several hours; this was followed by flushing with dry solvent. Flasks containing $[Fe(NCMe)_6]^{2+}$ and $P(OMe)_3$ solutions were attached to the syringe reservoirs *via* B.14 joints, and the solutions bled in under N_2.

Formation of the red species, identified as $[Fe(NCMe)_4\{P(OMe)_3\}_2]^{2+}$, was complete within 2 s after mixing, and was followed at 23 300 and 29 000 cm^{-1}, the absorption maxima. The spectrum of the species in the visible region was obtained by optical-density measurements at 20-nm intervals. Reaction traces were analysed using a standard computer program.[13] The estimated error of the observed rate constants was ±10%.

The overall formation constant of $[Fe(NCMe)_4\{P(OMe)_3\}_2]^{2+}$ was determined spectrophotometrically using a Beckman 5270 spectrometer and solutions in which $[Fe(NCMe)_6]^{2+}$ was 1.7×10^{-2} mol dm^{-3} and $P(OMe)_3$ was 8.5×10^{-3}, 1.7×10^{-2}, or 3.4×10^{-2} mol dm^{-3}. Molar absorption coefficients were those obtained from the stopped-flow spectrum. Under the conditions used, the decay of the red species was very slow.

The subsequent complexation steps were studied using MeCN solutions in which $[Fe(NCMe)_6]^{2+}$ was 3.4×10^{-3} mol dm^{-3} and $P(OMe)_3$ was in the range 0.11—0.86 mol dm^{-3}. A stock solution of $[Fe(NCMe)_6]^{2+}$ was prepared in the glove-box and aliquots transferred using syringes to several evacuable 10-mm Spectrosil cells,[2] which had been degassed and flamed out *in vacuo*. The solutions were degassed and appropriate quantities of $P(OMe)_3$ and MeCN, sufficient to make the total solution volume 5 cm^3, were added by vacuum distillation. Allowance was made for the volume of $P(OMe)_3$ added; however, the volume change on mixing $P(OMe)_3$ with MeCN was assumed to be zero. This, and the determination of the $[Fe(NCMe)_6]^{2+}$ aliquot, were the major sources of error. Reaction mixtures were held at 77 K until required, then rapidly warmed to room temperature and placed in the thermostatted cell holder of the spectrometer. Spectra over the range 280—600 nm were recorded at 2.5-min intervals, these being increased as the reaction progressed, and reactions were followed for 3—6 h depending on the $P(OMe)_3$ concentration.

We thank Mr. G. Anderson for experimental assistance and the S.R.C. and N.A.T.O. for financial support.

[1/579 *Received*, 10*th April*, 1981]

REFERENCES

[1] (*a*) E. L. Muetterties and J. W. Rathke, *J. Chem. Soc., Chem. Commun.*, 1974, 850; (*b*) P. Meakin, A. D. English, S. D. Ittel, and J. P. Jesson, *J. Am. Chem. Soc.*, 1975, **97**, 1254; (*c*) S. D. Ittel, F. A. Van Catledge, and J. P. Jesson, *ibid.*, 1979, **101**, 3874; (*d*) S. D. Ittel, A. D. English, C. A. Tolman, and J. P. Jesson, *Inorg. Chim. Acta*, 1979, **33**, 101; (*e*) A. Drummond, J. F. Kay, J. H. Morris, and D. Reed, *J. Chem. Soc., Dalton Trans.*, 1980, 284.

[2] C. J. Barbour, J. H. Cameron, and J. M. Winfield, *J. Chem. Soc., Dalton Trans.*, 1980, 2001.

[3] T. J. Huttemann, B. M. Foxman, C. R. Sperati, and J. G. Verkade, *Inorg. Chem.*, 1965, **4**, 950.

[4] See, for example, J. Burgess, 'Metal Ions in Solution,' Ellis Horwood Ltd., Chichester, 1978, chs. 11 and 12.

[5] R. J. West and S. F. Lincoln, *Aust. J. Chem.*, 1971, **24**, 1169.

[6] F. K. Meyer, K. E. Newman, and A. E. Merbach, *J. Am. Chem. Soc.*, 1979, **101**, 5588.

[7] F. K. Meyer, K. E. Newman, and A. E. Merbach, *Inorg. Chem.*, 1979, **18**, 2142; Y. Yano, M. T. Fairhurst, and T. W. Swaddle, *ibid.*, 1980, **19**, 3267.

[8] See, for example, D. B. Rorabacher, *Inorg. Chem.*, 1966, **5**, 1891.

[9] See, for example, G. H. Nancollas, 'Interactions in Electrolyte Solutions,' Elsevier, Amsterdam, London, and New York, 1966, ch. 1.

[10] C. A. Tolman, *J. Am. Chem. Soc.*, 1970, **92**, 2956; *Chem. Rev.*, 1977, **77**, 313.

[11] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' 2nd edn., Wiley, New York, 1961, p. 166.

[12] J. Burgess, *J. Chem. Soc., Dalton Trans.*, 1972, 1061; H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 2080; T. R. Sullivan, D. R. Stranks, J. Burgess, and R. I. Haines, *J. Chem. Soc., Dalton Trans.*, 1977, 1460.

[13] A. G. Lappin and A. McAuley, *J. Chem. Soc., Dalton Trans.*, 1975, 1560.