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THE PENTACYANONITROSYLFERRATE ION—V*. THE COURSE OF THE REACTIONS OF NITROPRUSSIDE WITH A RANGE OF THIOLS

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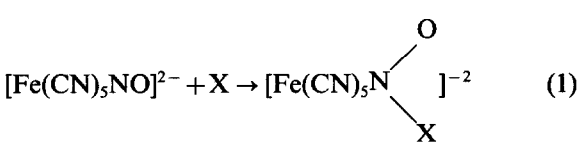
Abstract—Thiols RSH (RSH = MeSH, cysteine, N-acetylcysteine, 2-methylcysteine, N-acetyl-2-methylcysteine, penicillamine, N-acetylpenicillamine and glutathione) react with nitroprusside ($[Fe(CN)_5NO]^{2-}$, pentacyanonitrosylferrate(2−)) to give, via the intermediates $[Fe(CN)_5N(O)SR]^{3-}$ and $[Fe(CN)_5NO]^{3-}$, the pentacoordinate iron(I) complex $[Fe(CN)_4NO]^{2-}$. The fate of this complex depends crucially upon the reaction conditions; in the presence of oxygen, $[Fe(CN)_4NO]^{2-}$ can reform $[Fe(CN)_5NO]^{2-}$ to give an effective stoichiometry of RS^- to $[Fe(CN)_5NO]^{2-}$ substantially greater than 1 : 1; in the absence of oxygen and with a stoichiometric ratio of 1 : 1, the $[Fe(CN)_4NO]^{2-}$ follows a well established pathway to yield $[Fe(CN)_6]^{4-}$, Fe^{2+} and NO; in the absence of oxygen and with an excess of the RS^- ligand, substitution occurs at $[Fe(CN)_4NO]^{2-}$ to give firstly $[Fe(NO)_2(SR)_2]^-$ and subsequently $[Fe_2(SMe)_2(NO)_4]$ (where R = Me) or $[Fe_4S_3(NO)_7]^-$ (when R = H). For every R except R = H, decomposition of the initial adduct $[Fe(CN)_5N(O)SR]^{3-}$ yields the disulphide RSSR; when R = H, elemental sulphur is formed.

The kinetics of the reactions of thiols RSH and thiolate anions RS^- with the nitroprusside ion, pentacyanonitrosylferrate(2−) $[Fe(CN)_5NO]^{2-}$, have been rather extensively studied.[2–5] The initial step in the reaction is attack by the thiolate anion RS^- on the nitrogen atom of the nitrosyl ligand:[5] this is comparable to the initial step in the reactions of other oxygen-, nitrogen- and carbon-centred[6–15] nucleophiles with nitroprusside, eq. (1):



$$[Fe(CN)_5NO]^{2-} + X \rightarrow [Fe(CN)_5N(O)X]^{-2} \quad (1)$$

where X = ^-OH (ref. 6), ^-SH (ref. 2), NH_2R (refs 7, 8), ^-NHR (ref. 9), NHR_2 (ref. 10), $^-CHR_2$ (refs 1, 11–14), ^-SR (refs 3–5, 16, 17).

In some cases,[3] the primary intermediate $[Fe(CN)_5N(O)SR]^{3-}$ has been observed to decay to a paramagnetic species, characterized by $g = 2.024$, $A(^{14}N) = 15$ G (1N), which can also be obtained by reduction of nitroprusside electrochemically,[3] or by use of borohydride, ascorbic acid, quinol or dithionite,[3] or superoxide.[18] This paramagnetic species, commonly described in the literature as $[Fe(CN)_5NO]^{3-}$ (although formulations such as $[Fe(CN)_5NOH]^{2-}$ and $[Fe(CN)_5NO_2]^{5-}$ have also been suggested), is[19] in fact $[Fe(CN)_4NO]^{2-}$, presumably formed in every case by very fast[20] dissociation of $[Fe(CN)_5NO]^{3-}$. Apart from these observations[3] of $[Fe(CN)_4NO]^{2-}$, together with the identification[3] of the disulphide RSSR cor-

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responding to the initial thiol RSH when RSH was PhSH,[3] $PhCh_2SH$[3] or cysteine,[4] essentially nothing is known of the subsequent course of the reaction between nitroprusside and thiols.

In this paper we report the determination of the reaction stoichiometry and the final products, and the identification of a number of the intermediates, for a wide range of thiols.

RESULTS

Final products

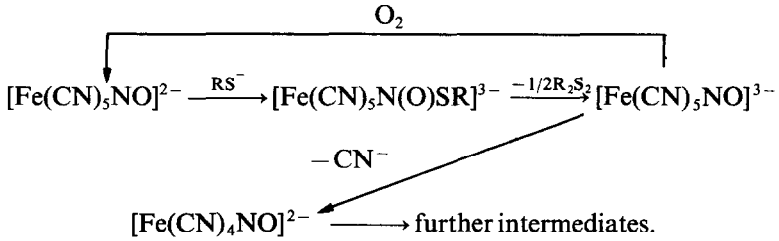
For all the thiols RSH examined in this study, except H_2S, the final products of similar reactions were the corresponding disulphide, identified in most examples by ^1H and ^{13}C NMR spectroscopy, and hexacyanoferrate(II) $[Fe(CN)_6]^{4-}$ again identified[21] by ^{13}C NMR spectroscopy. When H_2S was the thiol, $[Fe(CN)_6]^{4-}$ was again formed along with elemental sulphur. Nitrogen(II) oxide was identified as a product of the reactions of several thiols with nitroprusside.

The products and intermediates which were unambiguously identified are summarized, for each of the thiols studied, in Table 1.

Reaction stoichiometry

When the primary adduct $[Fe(CN)_5N(O)SR]^{3-}$ formed from nitroprusside and thiolate anions decomposes, the characteristic[3,4,5] purple colour fades: however if the thiolate is in excess, then aeration of the faded solution regenerates the purple adduct. The sequence of aeration, followed by fading of the newly purple solution, followed by further aeration can be repeated many times; in this way, nitroprusside has been made[4] to oxidize up to ten molar equivalents of cysteine to cystine.

We have confirmed these observations[4] and find from NMR titrations that, in air, typical stoichiometric ratios of thiolate: nitroprusside lie in the range 2:1 to 4:1. However, when oxygen is rigorously excluded, the reaction stoichiometry is precisely 1:1. The simplest rationalization of the effect of oxygen is in terms of eq. (2):



(2)

Table 1. Formation[a] of intermediates and products in the reactions of RS^- with $[Fe(CN)_5NO]^{2-}$

RSH	$[Fe(CN)_5N(O)SR]^{3-}$ λ_{max} (nm)	Intermediates $[Fe(CN)_4NO]^{2-}$	Intermediates $[Fe(NO)_2(SR)_2]^-$	Final products $[Fe(CN)_6]^{4-}$	Final products RSSR
H_2S	570	+	+[b]	+	[c]
MeSH	522	+	+[b]	+	[d]
Cysteine	522	+	−	+	[d]
N-acetylcysteine	522	+	+[e]	+	+
2-Methylcysteine	521	n.s.	−	+	+
N-acetyl-2-methylcysteine	520	+	+[e]	n.s.	n.s.
Penicillamine[f]	526	n.s.	−	+	+
N-acetylpenicillamine	525	+	+[e]	+	+
Glutathione[g]	520	+	−	+	+

[a] Product observed, +; product not observed, −; not studied, n.s.; $[Fe(CN)_4NO]^{2-}$ and $[Fe(NO)_2(SR)_2]^-$ identified by EPR spectroscopy; $[Fe(CN)_6]^{4-}$ and RSSR identified by ^{13}C NMR spectroscopy, except as noted.

[b] Observed only with excess of RS^-.

[c] Elemental sulphur (but not HSSH) isolated and identified by mass spectrometry.

[d] Water-insoluble RSSR isolated prior to identification.

[e] Observed as a minor product in reactions at 1:1 stoichiometry.

[f] 2,2-Dimethylcysteine.

[g] Ref. 30.

The reduced anion $[Fe(CN)_5NO]^{3-}$ is known[20] from pulse radiolysis work to be the primary product of electron attachment to nitroprusside, which furthermore undergoes[20] very rapid dissociation to yield $[Fe(CN)_4NO]^{2-}$. This latter cyanoferrate is that observed by EPR spectroscopy in the reactions of thiolates with nitroprusside (ref. 2 and Table 1), and probably arises by the same route; the $[Fe(CN)_5NO]^{3-}$ having been formed by the loss of $RS^{\bullet}$ or $\frac{1}{2}R_2S_2$ from the purple adduct $[Fe(CN)_5N(O)SR]^{3-}$.

The intermediate $[Fe(CN)_5NO]^{3-}$ is formed by a reaction between RS^- and $[Fe(CN)_5NO]^{2-}$ of 1 : 1 stoichiometry: in the absence of air it all decays to $[Fe(CN)_4NO]^{2-}$. However, in the presence of oxygen at least part of the $[Fe(CN)_5NO]^{3-}$ is oxidized, reforming $[Fe(CN)_5NO]^{2-}$ which can react with further RS^-, so giving an overall stoichiometry, in air, with the ratio RS^- : $[Fe(CN)_5NO]^{2-}$ greater than 1 : 1.

While the recycling back to $[Fe(CN)_5NO]^{2-}$ was observed with most of the thiols in Table 1 (and with homocysteine), no such recycling was observed with the sterically hindered thiols $HSCMe_2CH(NH_2)COOH$ (penicillamine) and $HSCEt_3$.

Identified intermediates

The initial adduct is[4] of type $[Fe(CN)_5N(O)SR]^{3-}$: for a wide range of thiols RSH, except for H_2S, the adduct has λ_{max} in the range 520–526 nm (Table 1). Thioglycolic acid and 2-mercaptoethanol gave[3] similar adducts having λ_{max} of 522 nm.

The hydrogen sulphide anion HS^- is a unique thiolate, because of the possibility of further proton loss from its initial adduct with nitroprusside. The kinetics of the reaction of HS^- with nitroprusside were interpreted[2] in terms of an initial species A, which was then converted to a second species B. The formation of A was first-order in each of nitroprusside and HS^-, while the conversion of A to B was first-order in A only, and was independent of both pH and HS^- concentration.[2] A and B were identified[2] as $[Fe(CN)_5N(O)SH]^{3-}$ and $[Fe(CN)_5NOS]^{4-}$, respectively, although λ_{max} for A, 570 nm, is markedly different from that of other $[Fe(CN)_5N(O)SR]^{3-}$ species (Table 1). Nor has the constitution of B been fully established.[22]

Loss of either $RS^{\bullet}$ or $\frac{1}{2}R_2S_2$ from the primary adduct $[Fe(CN)_5N(O)SR]^{3-}$ yields the known[20] $[Fe(CN)_5NO]^{3-}$, which in the absence of oxygen decays[20] to the paramagnetic $[Fe(CN)_4NO]^{2-}$.[23] When RSH is cysteine, the decay of the primary adduct $[Fe(CN)_5N(O)SR]^{3-}$ has been shown[4] to follow first-order kinetics: this suggests that the initial decay products are $[Fe(CN)_5NO]^{3-}$ and the thiyl radical $RS^{\bullet}$, eq. (3), but it has not yet proven possible to detect or trap such thiyl radicals in these reactions:

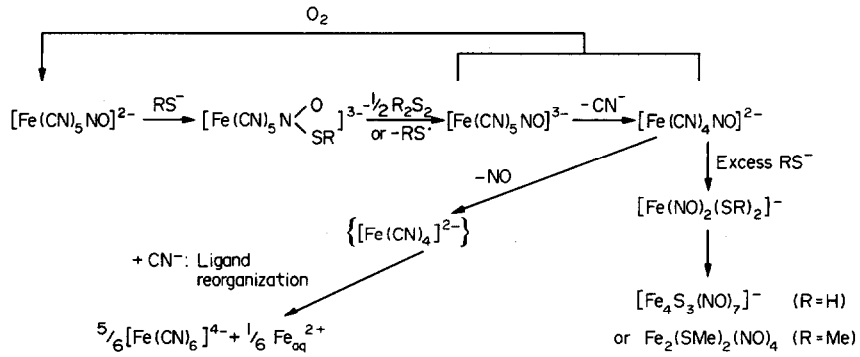
$$[Fe(CN)_5N(O)SR]^{3-} \rightarrow [Fe(CN)_5NO]^{3-} + RS^{\bullet}. \quad (3)$$

The square-pyramidal[23] five-coordinate complex $[Fe(CN)_4NO]^{2-}$ is substitution labile[24] and in the presence of a 10–20-fold molar excess of RS^- (for R = H or Me) the characteristic[19] EPR spectrum of $[Fe(CN)_4NO]^{2-}$ is rapidly replaced by those of the known[25] dinitrosyl complexes $[Fe(NO)_2(SH)_2]^-$ and $[Fe(NO)_2(SMe)_2]^-$; (R = H: $g = 2.027$, $A(^{14}N) = 2.7$ G, $A(^1H) = 0.5$ G; R = Me: $g = 2.027$, $A(^{14}N) = 2.1$ G, $A(^1H) = 2.1$ G). The resulting conversion of an $\{Fe(NO)\}^7$ complex to an $\{Fe(NO)_2\}^9$ complex is yet another example of the very easy interconversion of $[Fe(NO)]^{2+}$ and $[Fe(NO)_2]^+$ fragments.

The mononuclear dinitrosyls $[Fe(NO)_2(SH)_2]^-$ and $[Fe(NO)_2(SMe)_2]^-$ are known[25,26] precursors of tetranuclear $[Fe_4S_3(NO)_7]^-$ and dinuclear $Fe_2(SMe)_2(NO)_4$, respectively: on a preparative scale, similar oxygen-free reactions of $[Fe(CN)_5NO]^{2-}$ with an excess of HS^- or MeS^- gave isolated purified yields of $Na[Fe_4S_3(NO)_7]$ (when $RS^- = HS^-$, yield 26%) or $Fe_2(SMe)_2(NO)_4$ (when $RS^- = MeS^-$, yield 7.2%).

Similar paramagnetic species having g values slightly higher than the primary paramagnetic complex $[Fe(CN)_4NO]^{2-}$ have previously been observed[3] in reactions between $[Fe(CN)_5NO]^{2-}$ and $HOCH_2CH_2SH$, $HSCH_2COOH$ or PhSH: these species were not identified,[3] but the formulation $[Fe(CN)_5NHSR]^{3-}$ (containing the neutral radical ligand $RSNH^{\bullet}$) was suggested. We can now, with some confidence, reassign these in every case as $[Fe(NO)_2(SR)_2]^-$, having R = CH_2CH_2OH, CH_2COOH and Ph, respectively.

The observation noted above, that with an excess of HS^- nitroprusside yields $[Fe(CN)_4NO]^{2-}$ which in turn reacts with HS^- to give $[Fe(NO)_2(SH)_2]^-$, must call into question the published[2] interpretation of the kinetics of the reaction of $[Fe(CN)_5NO]^{2-}$ with HS^-: typical molar ratios of HS^- to $[Fe(CN)_5NO]^{2-}$ were[2] 80 : 1. Hence the interpretation[2] of species A and B as $[Fe(CN)_5N(O)SH]^{3-}$ and $[Fe(CN)_5NOS]^{4-}$, respectively, seems unlikely to be complete. Under the conditions used in the kinetic study,[2] we have identified, in succession $[Fe(CN)_4NO]^{2-}$, $[Fe(NO)_2(SH)_2]^-$ and $[Fe_4S_3(NO)_7]^-$, but we have no unambiguous evidence for the existence of $[Fe(CN)_5NOS]^{4-}$. The identified intermediates are summarized in Table 1.



Scheme 1.

Reaction mechanism

The overall mechanistic scheme for the reaction between nitroprusside and thiols is given in Scheme 1. In terms of this scheme, three distinct reaction pathways can be defined dependent upon the initial ratio of RS^- to $[Fe(CN)_5NO]^{2-}$ and upon the presence or absence of atmospheric oxygen.

(i) *Oxygen present.* Part or all of the $[Fe(CN)_5NO]^{3-}$ (or possibly $[Fe(CN)_4NO]^{2-}$ and CN^-) is oxidized back to $[Fe(CN)_5NO]^{2-}$. If a molar excess of RS^- over initial $[Fe(CN)_5NO]^{2-}$ is present, the reformed $[Fe(CN)_5NO]^{2-}$ will react with further RS^- to give an effective stoichiometric ratio of RS^- to $[Fe(CN)_5NO]^{2-}$ greater than 1 : 1.

(ii) *Oxygen absent and no initial excess of* RS^-. All of the $[Fe(CN)_4NO]^{2-}$ loses NO and after re-addition of the cyanide ion lost earlier and ligand reorganization, yields $[Fe(CN)_6]^{4-}$, together with Fe^{2+}_{aq}.

(iii) *Oxygen absent and* RS^- *present in excess.* Ligand substitution occurs in $[Fe(CN)_4NO]^{2-}$ to yield, after nitrosyl ligand migration[25] and redox disproportionation,[25] $[Fe(NO)_2(SR)_2]^-$.

With the single exception of the postulated intermediate, $[Fe(CN)_4]^{2-}$ arising from loss of NO from $[Fe(CN)_4NO]^{2-}$, all of the intermediates and products in Scheme 1 have been identified and characterized, mainly by us, but $[Fe(CN)_5NO]^{3-}$ and Fe^{2+}_{aq} by others.[20,27]

In Table 1, we summarize the identified intermediates and products for each of the thiols studied in the present work. In addition to the results of Table 1, we note that $[Fe(CN)_4NO]^{2-}$ was formed, although not identified as such,[3] when RSH was $HSCH_2CH_2OH$, $HSCH_2COO^-$, HSPh and $HSCH_2Ph$.

Kinetics

The kinetics of the initial adduct-forming step, eq. (4), have been studied by Wilkins[5] for a range of thiols, using temperature-jump methods and the values of k_f and k_d established.

$$[Fe(CN)_5NO]^{2-} + RS^- \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [Fe(CN)_5N(O)SR]^{3-}. \quad (4)$$

We have extended the range of thiols studied to include penicillamine $HSCMe_2CH(NH_2)COOH$, N-acetylpenicillamine and homocysteine $HSCH_2CH_2CH(NH_2)COOH$. The relaxations were effectively first-order and with nitroprusside in excess over the thiol the relaxation time τ is given by eq. (5):

$$\tau^{-1} = k_f[Fe(CN)_5NO]^{2-} + k_d. \quad (5)$$

The resulting values of k_f and k_d are given in Table 2 and confirm further that the variation of k_f and k_d with structural variation adjacent to the thiol centre is very slight. For all the thiols studied, here and elsewhere,[5] the overall range of k_f and k_d is small. In all cases k_f is of the order of 10^4 s^{-1} dm^3 mol^{-1}.

Table 2. Rate constants for adduct-forming equilibria

Thiol	pH	k_f (s^{-1} dm^3 mol^{-1})	k_d (s^{-1})
Penicillamine	11.2	1.50×10^4	3.90×10^3
N-acetylpenicillamine	11.2	1.75×10^4	2.55×10^3
Homocysteine	10.5	1.33×10^4	2.47×10^3

DISCUSSION

The course of the reaction between RS^- and $[Fe(CN)_5NO]^{2-}$ established above (Scheme 1) is clearly entirely different from those which have been described for other nucleophiles such as OH^-,[6] primary and secondary amines,[7-10] and simple carbanions.[11-14] In such cases the initial adduct $[Fe(CN)_5N(O)X]^{2-}$ arising from the addition of the nucleophile X to nitroprusside [eq. (1)] decomposes in a dissociation reaction giving $[Fe(CN)_5H_2O]^{3-}$ and XNO which undergoes further reaction. The eventual products from XNO are NO_2^- (when $X = OH^-$), ROH (when $X = RNH_2$),[7,8] R_2NNO (when $X = R_2NH$),[10] or $R_2C=NOH$ (when $X = {}^-CHR_2$).[11-14] For each of these nucleophile types, the nitrosyl ligand is incorporated into the final products: when $X = RNH_2$, the final products are ROH and N_2 where one atom of the each dinitrogen molecule arises from the nitrosyl ligand of $[Fe(CN)_5NO]^{2-}$, and the other atom from RNH_2.

In contrast, the reaction of $[Fe(CN)_5NO]^{2-}$ with RS^- does not generate any product which incorporates the nitrosyl ligand. A strict parallel with the reactions of amines and carbanions would suggest that the S-nitrosothiol, RSNO, is the primary product XNO. However, we have never observed such products, even from reactions using thiols like N-acetylpenicillamine which are known[28] to form highly stable S-nitroso derivatives. Rather, the reactions proceed as indicated in Scheme 1 and the nitrosyl ligand is liberated as neutral NO. For reactions *in vitro* in the absence of oxygen, the NO is lost from the reaction and is readily identified by IR spectroscopy. In reactions *in vivo*, the NO may be trapped, for example, by haem groups, as a nitrosylhaem.[29,30]

Now that the course of the reactions of thiols with nitroprusside have been delineated, it seems probable that several of the kinetic studies of these reactions[3-5] will require re-evaluation.

EXPERIMENTAL

Except where stated otherwise, thiols were purchased from Sigma and were used as received. NaSH and NaSMe were prepared by the reaction of metallic sodium with H_2S or Me_2S_2, in ethanol or liquid ammonia, respectively. A sample of Et_3CSH was kindly donated by Prof. Sir Derek Barton, FRS.

Preparation of 2-methylcysteine

A mixture of acetaldehyde (158 cm^3), hippuric acid (56.5 g) and sodium acetate (26.0 g) was refluxed in acetic anhydride (158 cm^3) for 3 h. The mixture was cooled and ice-cold water was added to precipitate 4-ethylidene-2-phenyl-5-oxazolone (44.1 g, 75%): δ (^1H) ($CDCl_3$ solution); 2.2 (d, 3H), 6.8 (q, 1H), 7.6–8.1 (m, 5H). A solution of oxazolone (39.7 g) in toluene (210 cm^3) was added slowly, at 5–10°C, to a solution formed from sodium metal (10.6 g) and benzyl mercaptan (25 cm^3) in dry methanol (200 cm^3). The mixture was stirred overnight and then acidified with aqueous HCl (Congo Red). The solvent was removed and the resulting syrup was dissolved in glacial acetic acid (500 cm^3) and refluxed for 1 h. The mixture was cooled to 4°C overnight and the resulting precipitate filtered off and washed successively with acetic acid and water to provide 1-(N-benzoylamino)-2-benzylthiobutyric acid (21.0 g, 30%). This was suspended in a mixture of 85% formic acid (325 cm^3), concentrated hydrochloric acid (325 cm^3), and water (325 cm^3), and the whole refluxed for 4 h. The solvent mixture was removed and the residue extracted with hot petroleum (b.p. 60–80°C) (2 × 250 cm^3) and then with hot water (2 × 250 cm^3). The aqueous extract was filtered, neutralized with ammonia and concentrated to 65 cm^3. Cooling this solution precipitated 1-amino-2-benzylthiobutyric acid (11.0 g, 77%): δ (^1H) ($CDCl_3$ solution); 1.3 (d, 3H), 2.1 (s, 2H), 3.4 (m, 1H), 3.7 (s, 2H), 5.0 (d, 1H), 7.3 (m, 5H).

The foregoing amino acid (2.0 g) was dissolved in a solution of sodium (0.83 g) in liquid ammonia (55 cm^3). Ammonium chloride (1.86 g) was added and the solvent removed. Concentrated hydrochloric acid (0.70 cm^3) was added and the solid residue extracted with ether (3 × 30 cm^3). The residue was then extracted with warm ethanol (3 × 15 cm^3). The ethanol was removed and replaced by 120 cm^3 of ether/ethanol (10:1 *v/v*), and the resulting solution was cooled overnight to yield 2-methylcysteine (0.31 g, 26%).

Instruments

NMR spectra were recorded on a Bruker AM-300 spectrometer, EPR spectra on a Bruker ER200D spectrometer with d-*t*-butyl nitroxide as the standard for the measurement of line positions, and electronic spectra on a Pye-Unicam SP8-100 spectrophotometer. Fast kinetics were measured using a Messenlager *T*-jump apparatus.

REFERENCES

1. A. R. Butler, A. M. Calsy and C. Glidewell, *J. Organomet. Chem.*, in press.
2. P. A. Rock and J. H. Swinehart, *Inorg. Chem.* 1966, **5**, 1058.

3. D. Mulvey and W. A. Waters, *J. Chem. Soc., Dalton Trans.* 1975, 951.
4. P. J. Morando, E. B. Borghi, L. M. de Schteingart and M. A. Blesa, *J. Chem. Soc., Dalton Trans.* 1981, 435.
5. M. D. Johnson and R. G. Wilkins, *Inorg. Chem.* 1984, **23**, 231.
6. J. H. Swinehart and P. A. Rock, *Inorg. Chem.* 1966, **5**, 573.
7. A. R. Butler, C. Glidewell, J. Reglinski and A. Waddon, *J. Chem. Res.* 1984, (S), 279, (M) 2768.
8. L. Dózsa, V. Kormos and M. T. Beck, *Inorg. Chim. Acta* 1984, **84**, 69.
9. R. Nast and J. Schmidt, *Z. Naturforsch. B* 1977, **23B**, 469.
10. J. Casado, M. Mosquera, M. F. Rodriguez Prieto and J. Vazquez Tato, *Ber. Bunsenges. Phys. Chem.* 1985, **89**, 735.
11. J. H. Swinehart and W. G. Schmidt, *Inorg. Chem.* 1967, **6**, 232.
12. S. K. Wolfe and J. H. Swinehart, *Inorg. Chem.* 1968, **7**, 1855.
13. N. Y. M. Iha and H. E. Toma, *Inorg. Chim. Acta* 1984, **81**, 181.
14. A. R. Butler, C. Glidewell, V. Chaipanich and J. McGinnis, *J. Chem. Soc., Perkin Trans 2* 1986, 7.
15. For a review: A. R. Butler and C. Glidewell, *Chem. Soc. Rev.*, in press.
16. K. Antal, I. Banyai and M. T. Beck, *J. Chem. Soc., Dalton Trans.* 1985, 1191.
17. M. Jakševac-Mikša, V. Hankonyi and V. Karas-Gašparec, *Z. Phys. Chem. (Leipzig)* 1980, **261**, 1041.
18. H. P. Misra, *J. Biol. Chem.* 1984, **259**, 12678.
19. C. Glidewell and I. L. Johnson, *Inorg. Chim. Acta* 1984, **132**, 145.
20. R. P. Cheney, M. G. Sijmic, M. Z. Hoffman, I. A. Taub and K.-D. Asmus, *Inorg. Chem.* 1977, **16**, 2187.
21. A. R. Butler, C. Glidewell, A. S. McIntosh, D. Reed and I. H. Sadler, *Inorg. Chem.* 1986, **25**, 970.
22. E. J. Baran and A. Müller, *Angew Chem. Int. Ed. Engl.* 1969, **8**, 890.
23. J. Schmidt, H. Kühr, W. L. Dorn and J. Kopf, *Inorg. Nucl. Chem. Letts* 1974, **10**, 55.
24. J. Fiedler and J. Mašek, *Inorg. Chim. Acta* 1984, **81**, 117.
25. A. R. Butler, C. Glidewell, A. R. Hyde and J. C. Walton, *Polyhedron* 1985, **4**, 797.
26. A. R. Butler and C. Glidewell, *Adv. Inorg. Chem.* 1988, **32**, 335.
27. N. G. Giniyatullin and Yu. M. Kargin, *Izv. Vysch. Uchebn. Zaved. Khim. Khim. Tekhnol.* 1976, **19**, 1668; *Chem. Abs.* 1977, **86**, 64862 r.
28. L. Field, R. V. Dilts, R. Ravichandran, P. G. Lenhert and G. E. Carnahan, *J. Chem. Soc., Chem. Commun.* 1978, 249.
29. A. R. Butler, C. Glidewell, I. L. Johnson and A. S. McIntosh. *Inorg. Chim. Acta* 1987, **138**, 159.
30. A. R. Butler, A. M. Calsy-Harrison, C. Glidewell, I. L. Johnson, J. Reglinski and W. E. Smith, *Inorg. Chim. Acta* 1988, **151**, 281.