Acyclic and Macrocyclic Schiff Base Complexes of Lanthanides and Actinides

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The work reviewed here is the result of a collaborative project designed to explore the interaction of lanthanides and actinides with acyclic and macrocyclic Schiff base ligands. The ligands are penta- and hexa-dentate in character and have present arrays of donors drawn from oxygen, nitrogen and sulphur atoms. The acyclic ligands are capable of allowing binuclear incorporation to occur; this feature was included in the study as is the area of selective metal extraction. A single ligand capable of removing two cations simultaneously would have cost benefit advantage over a ligand capable only of removing a single cation.

Complexes Derived from Acyclic Ligands

During the last few years we have developed a series of ligands capable of incorporating one, or two, metal cations derived from the reaction of α,ω-alkanediamines with β-triketones or β-ketophenols. These ligands have been collectively termed Compartmental Ligands [1] (Fig. 1). They provide adjacent, dissimilar donor sets capable of forming mononuclear positional isomers, homobinuclear and heterobinuclear complexes (Fig. 2). These ligands have been exploited in the formation of a wide range of transition metal complexes and we here describe the complexation properties of ligands, derived from
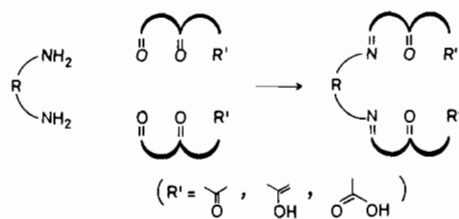

Fig. 1. Synthesis of compartmental ligands.

β-ketophenols and α,ω-alkanediamines, towards dioxouranium(VI).

Mononuclear positional isomers
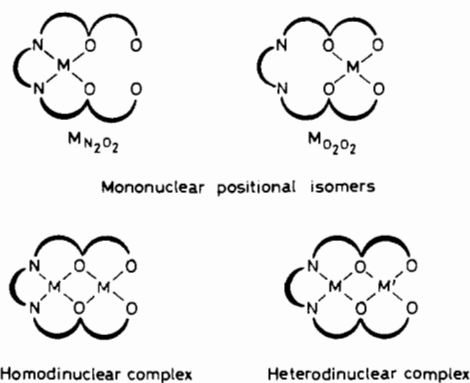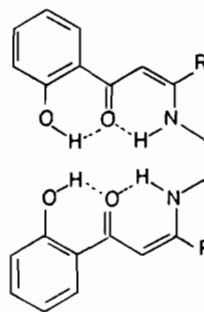
Homodinuclear complex   Heterodinuclear complex

Fig. 2.

(i) Mononuclear Complexes

Mononuclear complexes of ligands I and II were prepared by stoichiometric reaction of the ligand with dioxouranium(VI) ethanoate. The complexes were of the $UO_2(H_2-L)_{O_2,O_2}$, $H_2O(III)$ and the site
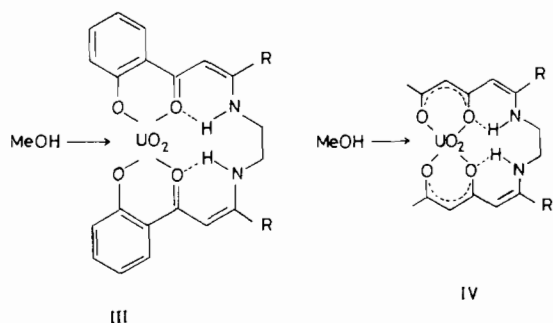

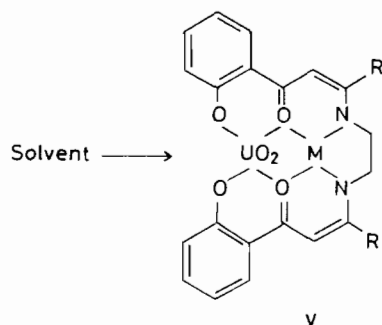I , R = CH₃ , H₄– A

II , R = C₂H₅ , H₄– B

occupancy is indicated by i.r. and by analogy with the complex (IV) for which an X-ray crystal structure is available [2]. The uranium(VI) is seven coordinate, this being achieved through interaction with the

donor atoms of the outer set and a molecule of solvent.

Fig. 3. The Cu environment in (V)-CuUO$_2$, 2 dmso.

(ii) Binuclear Complexes

Two types of binuclear complex are available, homobinuclear and heterobinuclear, and for the latter there is also the opportunity for positional isomerism to occur. However the dioxouranium(VI) cation has been found to occupy only the outer donor set and so it is a relatively straightforward matter to prepare heterobinuclear complexes, V, in which M = Cu or Ni. The complexes may be synthesised either by

Fig. 4. The Ni environment in (V)-NiUO$_2$, dmso.

taking the mononuclear dioxouranium(VI) complex and reacting it with the appropriate metal ethanoate, or by taking the mononuclear transition metal complex (having -N$_2$O$_2$ donor occupancy) and reacting it with dioxouranium(VI) ethanoate. The X-ray crystal structures of the UO$_2$·Cu [3] and UO$_2$·Ni [4] complexes of I have been solved. The crystals were obtained from dmso and for each complex the dioxouranium(VI) moiety lies in the -O$_2$O$_2$ set and is further bound to a molecule of dmso. The transition metal environments are unusual; the nickel(II) atom is four-coordinated but severely distorted with a trigonal bipyramidal environment having an empty site (Fig. 4), and the copper(II) atom is pentacoordinated (having a dmso of solvation) and there is a slight deviation from a square pyramidal geometry (Fig. 3).

The origin of the distortions is not entirely clear, but if it is a reproducible phenomenon, then it provides the interesting possibility of using the dioxouranium(VI) moiety to induce unusual, and possibly
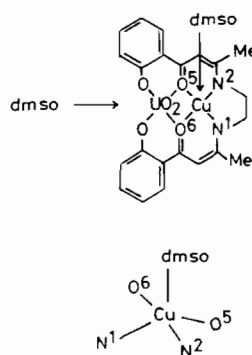
entatic, geometries at the second metal ion in a binuclear complex. Accordingly the crystal structure of the mononuclear precursors were undertaken. The structure of Ni(H$_2$-A)$_{N_2O_2}$ shows the nickel(II) to be square planar [5], and the structure of a related copper(II) complex [6], in which the bridging unit is cyclohexyl-, has a definite tetrahedral twist (14°).

The latter structure was solved as it had proved not possible to grow suitable crystals of Cu(H$_2$-A)$_{N_2O_2}$. The structure of UO$_2$(H$_2$-A)$_{O_2O_2}$, dmf shows the uranium atom to be in a pentagonal bipyramidal geometry with a solvent molecule providing the seventh donor. The uranyl(VI) ion occupies the outer O$_2$O$_2$ compartment which is inclined by 19° with respect to the inner N$_2$O$_2$ site. The five equatorial oxygen atoms are coplanar within ±0.1 Å as well as the four N$_2$O$_2$ atoms [7].

Thus the inner compartment N$_2$O$_2$ is not distorted in this structure, quite different from what is found for the inner site in (V)NiUO$_2$, dmso. This suggests that it is the addition of nickel(II) which gives a distortion in the binuclear complex. In the copper(II) complex it is possible that this also occurs as a first step, especially as the mononuclear complex is already tetrahedrally distorted, but that coordination of dmso occurs to give the more favourable square pyramidal geometry. One problem is that the com-
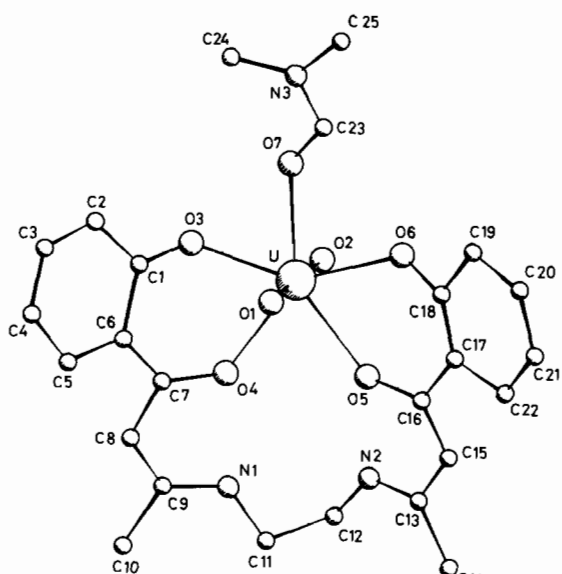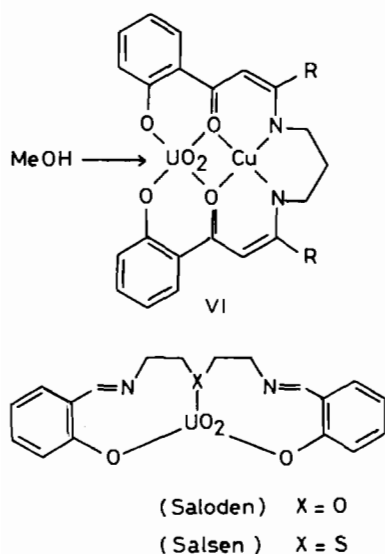
Fig. 5. The structure of $UO_2(H_2\text{-}A)_{O_2O_2}$ dmf.

pounds have necessarily been recrystallized from different solvent systems—dmso (heterobinuclear), dmf (uranyl), $CHCl_3$/EtOH (copper, nickel)—and this may influence the crystal growth. In contrast the structure of the heterobinuclear complex VI, in which there is an extra methylene group in the bridge allowing for an increased flexibility of the ligand the copper(II) is in a square planar environment [8].
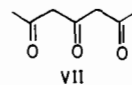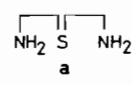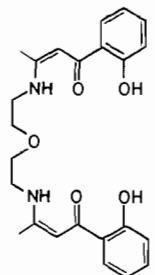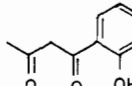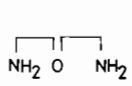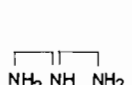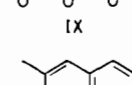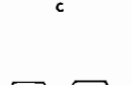
Studies on the related Schiff base complexes, UO_2(saloden) [9] and UO_2(salsen) [10] have shown that if the bridging unit is extended to include a further donor atom then a seven coordinated uranium complex results. This suggested that the incorporation of facultative bridges into compartmental ligands could yield homobinuclear complexes of uranium in which the dioxouranium(VI) could enter both com-

partments of the ligand and achieve seven coordination in each. No homobinuclear complexes of dioxouranium(VI) were prepared from ligands I and II, presumably because of the restricted size of the inner compartment.

A series of mononuclear complexes were prepared first *via* stoichiometric reaction of the ketoprecursor, facultative ligand and dioxouranium(VI) ethanoate using metal template techniques (Table I) [11]. The mononuclear complexes derived from VII showed no free carbonyl peaks in the i.r. and so were assigned $-O_2O_2$ occupancy as in IV. By analogy the mononuclear complexes of VIII–X were assigned outer occupancy and this is seen as a reflection of the relative hard and soft character of the available donor sites. The mononuclear complexes all retain one molecule of solvent, water or ethanol, depending upon the precise reaction conditions, and this would assist in the achievement of seven coordination by the uranium in the outer four donor atom set.

TABLE I.

Chetoprecursor	Facultative amine	Representative product

Homobinuclear dioxouranium(VI) complexes have been prepared from systems VII (b–d) and VIII (b–d) by template procedures, and for the systems IX (a–d) and X (b) by addition of LiOH and dioxouranium(VI) ethanoate either to the free ligand or to the mononuclear precursor. The complexes show retention of a mole of solvent as with the mononuclear precursors.
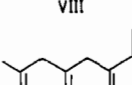
Recently the internal site of the binucleating ligand was enlarged with the addition of a phosphorus donor atom, and the heptadentate chelating compounds:

have been synthesized by the reaction of *o*-aceto-acetylphenol or 3-formylsalicylic acid with bis(3-aminopropyl)phenylphosphine [12].

With these ligands, binuclear uranyl(VI) complexes have been prepared and a structure of the type:

has been suggested, where a uranyl(VI)—phosphine bond is present, analogously to what is proposed for the uranyl(VI) complex with the ligand:

(H₂L)

This complex, $UO_2(L)$, is stable in air and apparently does not change with time. The mass spectrum shows a very intense peak due to the parent P^+ ion at 699 m/e. During the recrystallization an oxidation of the phosphine group to phosphine oxide occurs; the new complex obtained, $UO_2(L')$, has a different i.r. spectrum, especially in the ν_{P-O} region, and is non-volatile also under drastic conditions.

In $UO_2(L')$ the five donor atoms of the ligand are equatorially bonded to the uranyl group to form discrete, monomeric molecules with the seven coordinated metal in the usual distorted pentagonal bipyramidal coordination geometry. The molecule lies across a crystallographic mirror plane which contains the uranyl group and the PhPO fragment. The five coordinated atoms form a puckered pentagon where the oxygen atoms are slightly displaced above and the nitrogen atoms below the equatorial mean plane.

Fig. 6. The structure of $UO_2(L')$.

For the binuclear uranyl(VI) complexes, a similar behaviour towards oxidation of the phosphinic group can be supposed.

Complexes Derived from Macrocyclic Ligands

The facile generation of macrocyclic Schiff bases in the presence of alkaline earth metal cations [13] has led to an interest in the use of lanthanide cations as templating agents in similar circumstances. The comparable ion size suggests that such reactions should be successful.

Complexes of the 18-membered hexaazamacrocycle XI have been reported but were only obtained from $La(NO_3)_3$, $La(ClO_4)_3$ and $Ce(NO_3)_3$ [14, 15]. The heavier lanthanide cations were found to be effective as templating agents in the synthesis of the smaller 14-membered hexaazamacrocycle, XII [16]. The complexes obtained were of 1:1 stoichiometry and had the general formula (m/c) M(anions)₃.

Our work has focused on the reaction of pyridine-2,6-dicarbaldehyde or furan-2,5-dicarbaldehyde and α,ω-alkanediamines in the presence of lanthanide ions as templates.

TABLE II. Comparison between the Ionic Radii of Lanthanides and Some Alkaline Earth Metals [23].

Name	Symbol	Ionic radii (A)	Name	Symbol	Ionic radii (A)
Magnesium	Mg^{II}	0.78	Europium	Eu^{III}	0.950
Calcium	Ca^{II}	1.00	Gadolinium	Gd^{III}	0.938
Strontium	Sr^{II}	1.16	Terbium	Tb^{III}	0.923
Barium	Ba^{II}	1.36	Dysprosium	Dy^{III}	0.908
Lanthanum	La^{III}	1.061	Holmium	Ho^{III}	0.894
Cerium	Ce^{III}	1.034	Erbium	Er^{III}	0.881
Praseodymium	Pr^{III}	1.013	Thulium	Tm^{III}	0.869
Neodymium	Nd^{III}	0.995	Ytterbium	Yb^{III}	0.859
Samarium	Sm^{III}	0.964	Lutetium	Lu^{III}	0.848

All of the lanthanide cations, except Pm, were found to be effective as templates in the synthesis of macrocyclic complexes from pyridine-2,6-dicarbaldehyde and 1,2-diaminoethane. It was anticipated that all of the complexes would be of the hexaazamacrocyclic ligand, XIII, and would be of the general form $(m/c)M(anions)_3$. The i.r. spectra of the complexes of the heavier lanthanides (Nd → Lu, except Eu, Pm), however, were different from those for the complexes of the lighter lanthanides (La → Pr, and Eu). The spectra exhibited a complete absence of bands due to carbonyl or primary amines in all cases, but for the former group a distinctive band was detected at *ca.* 3220 cm^{-1}, indicative of a secondary amine group. The addition of a water molecule across an imine group would lead to formation of the carbinolamine species, XIV, and the occurrence of such an addition was supported by ^{13}C and ^{1}H n.m.r. spectral data.

XIII   XIV
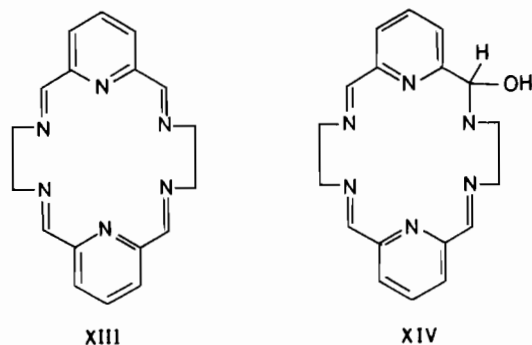
The ^{1}H n.m.r. spectrum of La^{3+} complex of XIII was run in d$_6$-dmso and showed the expected simple spectrum, (δ = 8.93 (s, 4H, CHN), 8.17 (d, 4H, H$_3$(pyr)), 8.45 (t, 2H, H$_4$(pyr)) and 4.07 (s, 8H, -CH$_2$CH$_2$-) ppm), and the ^{13}C n.m.r. gave peaks at 165.1 (imine C), 150.1 (C$_1$(pyridine)), 142.3 (C$_3$-(pyridine)), 129.1 (C$_2$(pyridine)), and 59.4 (ethylene bridge C's) ppm. The corresponding spectra for the Lu^{3+} complex of XIII are more complex and indicate an equilibrium in solution between XIII and XIV.

There are four singlet signals at δ = 9.10, 9.02, 8.98, and 8.93 ppm which correspond to the three -CH=N protons in XIV and to the single -CH=N protons in XIII. Furthermore the pyridinic region shows seven signals and there are additional multiplets in the region for the ethylenic bridge protons. A doublet is observed at δ = 5.60 ppm (J = 10.3 Hz) assignable to the carbinolamine signal ($>$CHOH in XIV) and a broad singlet is found at δ = 7.48 ppm due to the $>$NH proton in XIV. Addition of D$_2$O removes the latter signal and collapses the doublet to a singlet as coupling with the $>$NH is removed.

The ^{13}C n.m.r. spectrum is again more complex and indicates two types of macrocycle are present; one set of signals corresponds to those described for the La^{3+} complex of XIII and there are further peaks for the non-symmetrical macrocycle at 164.5, 164.3 and 163.9 ppm (imine C's), 162.4, 152.1, 152.0, 140.8, 128.9, 128.8, 126.8 and 124.9 ppm (pyridine C's), 80.8 ppm ($>$CHOH and 59.0, 58.9 and 57.5 ppm (ethylenic bridge C's)) [17].

Attempts were made to obtain crystals for X-ray analysis and in the case of the samarium complex were successful. However the band present in the i.r. of the bulk sample at 3210 cm^{-1} had disappeared and a new band was present at 3560 cm^{-1}. This band can be assigned to a Sm—OH group, and the crystal structure shows that the complex analysed is (XIII) Sm(OH)(NO$_3$)$_2$, H$_2$O [18].

The samarium cation is enclosed in the cyclic ligand and coordinated to the six nitrogen atoms as well as to a bidentate nitrate anion, a water molecule and a hydroxide anion. The coordination geometry is best described as an irregular antiprism capped on its 'square' faces by the pyridinyl-nitrogen atoms.

For the lighter, and larger, lanthanide cations the preferred products are those involving the tetraimine (XIII), (XIII)M(NO$_3$)$_3$, whereas for the heavier and smaller lanthanide cations the modified ligand
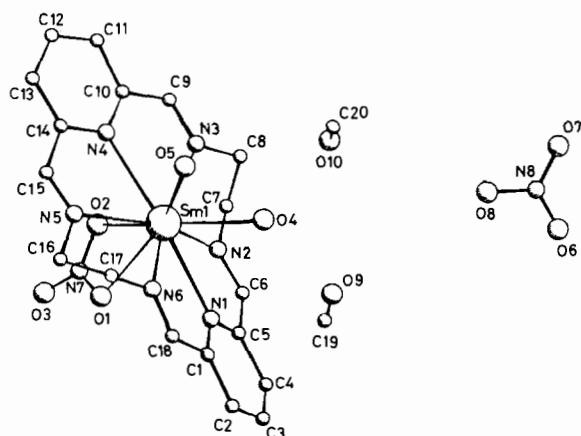
Fig. 7. The structure of (XIII) Sm(OH)(NO₃)₂, H₂O.

(XIV) is preferred. It is possible that in order to incorporate these latter ions the cavity size must be contracted to accompany the lanthanide contraction and this is done by making the ligand more flexible by addition of water, thus allowing it to bend round the cation. This effect has been noted in d-block transition metal chemistry. However it is also likely that as on heating to effect dissolution in water prior to recrystallisation a higher temperature is reached than in the original reaction in ethanol, the reaction moves on the completion and the ligand XIII results. The stabilisation of the carbinolamine (XIV) therefore represents the stabilisation of a reaction intermediate *via* the facile coordination of the smaller lanthanide cations.

The samarium complex is also hydrolysed on recrystallisation; it is not immediately obviously why this is required unless a reduction in samarium coordination number is accompanied by a radius contraction but this seemingly facile hydrolysis of lanthanium nitrate complexes has been observed by us in related systems which contain either compartmental, or macrocyclic ligands [19].

The reaction of furan-2,5-dialdehyde with lanthanium nitrates and 1,2-diaminoethane gave rise to 1:1 complexes of the macrocycle, XV, for the lighter lanthanides (La → Sm, except Pm) and are of
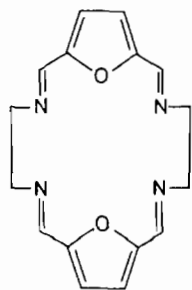
XV

the general form (m/c) $Ln(NO_3)_3$ [20]. For the heavier lanthanides the m.s. indicates that the macrocyle is present, but the best fit analyses indicate complexes having present three metal ions and two units of macrocycle, e.g. $Gd_3L_2(NO_3)_9 \cdot 4H_2O$. Recrystallisation of these complexes led to decomposition, in contrast to the pyridine-containing species, and the ^1H n.m.r. showed that the ring stayed intact in solution. This suggested that on redissolution the lanthanide is leached from the macrocycle which then, on attempted isolation, breaks down.

The ^1H n.m.r. of $La(XV)(NO_3)_3$ run immediately after the dissolution in d_6-dmso gave peaks at $\delta =$ 8.58 (s, 4H, -CHN), 7.37 (s, 4H, H(furan)), and 4.00 (s, 8H, -CH$_2$CH$_2$-) ppm. On standing a signal corresponding to a second species developed and this was attributed to the free macrocycle. After about one hour only these signals remained at $\delta = 8.25$, 6.88 and 3.90 ppm.

Macrocyclic complexes (XVI) were also obtained from the reaction of furan–2,5-dicarboxaldehyde and 1,3-propane–diamine in the presence of Ln-(NO$_3$)$_3$ (Ln = La–Pr); the m.s. showed parent peaks corresponding to the free macrocycle. For the heavier lanthanides intractable oils were recovered.

These complexes can be used in transmetallation reactions as can the alkaline earth metal analogues [21]. The reaction of $La(XV)(NO_3)_3$ with Cu-(ClO$_4$)$_2$ in ethanol gave a green precipitate of the homobinuclear copper(II) $Cu_2(XV)(ClO_4)_3OH$, 2H$_2$O, previously obtained from a barium source [22]. Such dicopper(II) complexes may be useful in the speculative modelling of the bimetallobiosite in copper-containing proteins such as oxyhaemocyanin and the blue copper oxidases.

Acknowledgements

References

1 U. Casellato, P. A. Vigato, D. E. Fenton and M. Vidali, *Chem. Soc. Rev., 8*, 199 (1979).
2 R. Graziani, M. Vidali, U. Casellato and P. A. Vigato, *Acta Cryst., B32*, 1681 (1976).
3 R. Graziani, M. Vidali, U. Casellato and P. A. Vigato, *Transition Metal Chem., 3*, 239 (1978).
4 R. Graziani, M. Vidali, U. Casellato and P. A. Vigato, *Transition Metal Chem., 3*, 99 (1978).
5 N. A. Bailey, S. M. Davison, J. R. Elliot, D. E. Fenton, E. Godbehere, S. K. Holdroyd and C. Rodriguez de Barbarin, submitted for publication.
6 N. A. Bailey, K. C. Cox, C. P. Falshaw, D. E. Fenton, S. L. Grundy, P. Haigh and C. A. Phillips, *J. Chem. Soc., Dalton Trans.*, in press.
7 U. Casellato, R. Graziani and P. A. Vigato, unpublished results.
8 N. A. Bailey and C. Rodriguez de Barbarin, personal communication.

9 A. M. Brock, D. H. Cook, D. E. Fenton, G. Bombieri, E. Forsellini and F. Benetollo, *J. Inorg. Nucl. Chem., 40*, 1551 (1978).

10 D. E. Fenton, P. A. Vigato, U. Casellato, R. Graziani and M. Vidali, *Inorg. Chim. Acta, 51*, 195 (1981).

11 R. Coombes, D. E. Fenton, P. A. Vigato, U. Casellato and M. Vidali, *Inorg. Chim. Acta, 54*, L155 (1981).

12 U. Casellato, P. A. Vigato, S. Tamburini, S. Sitran and R. Graziani, *Inorg. Chim. Acta, 95*, 147 (1984).

13 D. H. Cook and D. E. Fenton, *J. Chem. Soc., Dalton Trans., 266* and *810* (1981).

14 J. D. J. Backer-Dirks, C. J. Gray, F. A. Hart, M. B. Hursthouse and B. A. C. Schoop, *J. Chem. Soc., Chem. Commun., 774* (1979).

15 W. Radecka-Paryzek, *Inorg. Chim. Acta, 45*, L147 (1980).

16 W. Radecka-Paryzek, *Inorg. Chim. Acta, 52*, 231 (1981).

17 K. K. Abib and D. E. Fenton, unpublished results.

18 K. K. Abib, D. E. Fenton, U. Casellato, P. A. Vigato and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 351 (1984).

19 K. K. Abib and D. E. Fenton, *Inorg. Chim. Acta, 94*, 73 (1984).

20 K. K. Abib and D. E. Fenton, *Inorg. Chim. Acta, 95*, 119 (1984).

21 S. M. Nelson, *Pure and Appl. Chem., 52*, 2461 (1980).

22 S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 388 (1980).

23 R. D. Shannon and C. T. Prewitt, *Acta Cryst. B25*, 925 (1969).