Mononuclear Gold(I) and Heteronuclear Gold(I)—Palladium(II) Bibenzimidazolate Complexes with New Coordination Modes of the Ligand

R. USON, J. GIMENO, J. FORNIES, F. MARTINEZ and C. FERNANDEZ

Department of Inorganic Chemistry, University of Saragossa, Saragossa, Spain

Received March 16, 1982

Metathetic reactions of gold(I) halide complexes and the potassium salt of 2,2'-bibenzimidazol afford binuclear bibenzimidazolate gold(I) complexes with the general formula $\{Au_2L_2\}(\mu$ -BiBzIm) $L = PPh_3$, PBu_3^n , $P(OMe)_3$; $L_2 = 1,1$ -bis(diphenylphosphine)methane (dppm), 1,2-bis(diphenylphosphine)ethane (dppe). These complexes are Lewis bases and can be used as precursors for the synthesis of tri and tetranuclear cationic gold(I) complexes, or trinuclear gold(I) and palladium(II) complexes where the bibenzimidazolate anion is acting as bridging tetranuclear ligand. An hexanuclear gold(I)-palladium-(II) complex is also described.



Introduction

Recently we have shown that the bibenzimidazolate anion, $BiBzIm^{2-}$, can act as tetradentate bridging ligand between two metal centres

$$M \Big\langle {}_{N}^{N} \Big \langle {}_{N}^{N} \Big \rangle \Big\rangle^{N} = \left[\left(\bigcup_{N}^{N} \Big \rangle \Big)^{2^{2}} = \left[\left(\bigcup_{N}^{N} \Big \rangle \Big \rangle \Big)^{2^{2}} \right]^{2^{2}} = \left[\left(\bigcup_{N}^{N} \Big \rangle \Big)^{2^{2}} \right)^{2^{2}} = \left[\left(\bigcup_{N}^{N} \Big \rangle \Big)^{2^{2}} \right]^{2^{2}} = \left[\left(\bigcup_{N}^{N} \Big \rangle \Big]^{2^{2}} \right]^{2^{2}} = \left[\left(\bigcup_{N}^{N} \Big]^{2^{2}} \right]^{2^{2}} = \left[\left(\bigcup_{N}^{N}$$

thus giving rise to the formation of stable binuclear Au(III), Mn(I) and Pd(II) complexes [1-3]. Moreover, owing to its very nature a higher versatility may be expected for this ligand. In consequence we endeavoured to study new coordination modes of the BiBzIm²⁻ group.

In the present paper we describe the synthesis and properties of novel binuclear Au(I) complexes (A), which, behaving as potential mono or bidentate ligands, allow the preparation of different types of tri- and tetranuclear Au(I) complexes (B), (C), trinuclear hetero-atomic Au(I)-Pd(II) complexes (D), as well as an hexanuclear Au(I)-Pd(II) complex (E). All of them exhibit new types of coordination of the BiBzIm²⁻ ligand.

Some of these results have been the subject of a preliminary communication [4].

Results and Discussion

Metathetic reactions at room temperature between dichloromethane solutions of gold(I) halide complexes and the potassium salt of 2,2'-bibenzimidazol (H₂BiBzIm), according to eqn. 1

2 AuClL + K₂BiBzIm
$$\rightarrow$$
 (AuL)₂(μ -BiBzIm) + 2 KCl
(1)
L = PPh₃(I), PBuⁿ₃(II), P(OMe)₃(III)

lead to solutions, from which can be isolated binuclear gold(I) complexes with the bibenzimidazolate anion acting as a bidentate ligand bridging the two Au atoms. The analogous complexes $[(L-L)Au_2](\mu$ -BiBzIm) (L-L = dppm(IV), dppe(V))are similarly obtained as insoluble precipitates.

These complexes, which still contain two potential nitrogen donor atoms, behave as Lewis bases and can be used as precursors for the preparation of tri- and tetranuclear complexes.

Trinuclear Complexes

The addition of [(dppm)Au₂](µ-BiBzIm) (IV) to dichloromethane solutions of binuclear palladium-

							-	
	Complexes	%С	%Н	%N	%Au	M.W.	₀ W∨	M.P. °C
I	$[(Ph_3P)_2 Au_2] (\mu-BiBzIm)$	51.77	3.31	4.75	33.77	1149		300
		(52.19)	(3.33)	(4.87)	(34.23)	(1150.8)		٦
П	[(Bu ⁿ P) ₂ Au ₂] (µ-BiBzIm)	45.36	6.20	5.56	37.40	998		210 ^a
III		(44.29)	(6.06) 2.00	(5.43) 5.45	(38.23)	(1030.8)		166
III	{[(MeO)3r]2Au2}{(#-BIBZIII)	21.97 (27.45)	5.09 (2.99)	0.4.3 (6.40)	(45.07)	040 (874.3)		601
IV	$[(dppm)Au_2](\mu-BiBzIm)$	47.20	3.11	5.69	39.41	Ð		265 ^d
		(46.37)	(2.99)	(5.54)	(38.99)	c		τ
۷	[(dppe)Au ₂](µ-BiBzIm)	45.64	3.16	5.65	36.95	\$		2304
Λ1	[[r@hp] 16big-rm].cm].	(46.90) 47 12	(3.14) 3 14	(5.47) 3.36	(38.46) 22.52		149	248
		(47.77)	(3.12)	(3.27)	(23.04)			
ΝII	(dppm)Au ₂ (<i>u</i> -BiBzIm)PdCl ₂	39.71	2.75	4.97		Ð		$270^{\mathbf{d}}$
		(39.42)	(2.52)	(4.71)				٦
VIII	$(dppm)Au_2(\mu-BiBzIm)Pd(C_6F_5)Cl$	40.62	2.50	4.30		1529		268 ^a
		(40.95)	(2.27)	(4.24)		(1319.5) e		poor
XI	(dppm)Au ₂ (µ-BiBzIm)PdBr ₂	37.65	2.55	5.43		,		- 097
~	(dunm) \ 1 [BiBa[m]D4(C E].	(20-06) 17 80	(CC.2) 2 5 7	(4.20) 3.67		1461		225d
<		42.18)	3.32 (2.06)	3.86)		(1451.1)		24
ХІ	$(dppm)Au_2(\mu-BiBzIm)Pd(C_6Cl_5)_2$	38.55	2.57	3.13		÷		254 ^d
		(37.89)	(1.85)	(3.46)				τ
XII	[(dppm)Au ₂ (μ-BiBzIm)Pd(acac)]ClO ₄	40.47	3.07	4.09			91	228 ⁴
		(40.16)	(3.42)	(4.26)				þ
IIIX	[(dppm)Au ₂ (µ-BiBzIm)Pd(C ₆ F ₅)(PPh ₃)]ClO ₄	44.83	2.78	3.09			83	300~
1117		(45.97)	(2.73)	(3.40) 2.44	16 78		1 80	785
	1/11 1131)4 Aud 1 (m. D.D. C.I.O.d.)2	(45.54)	(3.02)	(2.47)	(17.37)			2024
xv	{[(dppm) ₂ Au ₄] (<i>µ</i> -BiBzIm)}(ClO ₄) ₂	39.51	2.77	2.69	38.81		204	300
		(38.68)	(2.63)	(2.81)	(39.64)			T
IVX	[(dppm)Au ₂ (µ-BiBzIm)Au ₂ (PPh ₃) ₂](ClO ₄) ₂	42.90	2.77	3.12	37.23		185	225 ^u
		(42.43)	(2.84)	(2.63)	(37.03)			
IIVX	[(dppm)Au ₂ (μ-BiBzIm)Au ₂ (PBu ₃) ₂](ClO ₄) ₂	37.20	3.68	3.47	39.05		190	175
		(37.69)	(4.21)	(2.79)	(39.24)			τ
IIIAX	$[(dppm)Au_2(\mu-BiBzIm)Au_2\{P(OMe)_3\}_2](ClO_4)_2$	36.36	2.85	3.61	42.81		177	210~
		(36.98)	(2.61)	(3.02)	(42.56)			b -25
XIX	$[\{(dppm)Au_2(\mu-BiBzIm)Pd\}_2(\mu-BiBzIm)](CIO_4)_2$	42.41	2.74	6.35			153	265~
		(41.45)	(2.54)	(6.30)				
^a Calculated va	ilues are given in parenthesis. $b_{\Omega}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, acetone	solutions.	^c Not soluble eno	ugh for determ	nation. ^d Dec	omposes.		

TABLE I. Analytical, Conductance and Molecular Weight Data for the New Complexes.^a

92

(II) halide complexes gives rise to the cleavage of the halide bridges (eqns. 2, 3)

$$(IV) + \frac{1}{2}Q_{2}[Pd_{2}(\mu - X')_{2}(C_{6}X_{5})_{4}] \rightarrow$$

$$(dppm)Au_{2}(\mu - BiBzIm)Pd(C_{6}X_{5})_{2} + QX' \qquad (2)$$

$$\mathbf{X} = \mathbf{F}; \mathbf{X}' = \mathrm{Br}(\mathbf{X}); \mathbf{X} = \mathbf{X}' = \mathrm{Cl}(\mathbf{XI}); \mathbf{Q} = \mathrm{NBu}_{4}^{\mathrm{n}}$$

$$(IV) + \frac{1}{2} Q_2[Pd_2(\mu-Br)_2Br_4] \rightarrow$$

$$(dppm)Au_2(\mu-BiBzIm)PdBr_2 + QBr \qquad (3)$$

and to the formation of the corresponding heteronuclear gold(I)-palladium(II) derivatives (complexes IX-XI; Table I).

The basicity of the binuclear amido gold(I) complexes allows the displacement of poorly coordinating ligands in processes such as the following (eqns. 4, 5)

(IV) + trans-PdCl₂(tht)₂
$$\rightarrow$$

(dppm)Au₂(μ -BiBzIm)PdCl₂ + 2 tht (4)

(I) + Au(OClO₃)(PPh₃) \rightarrow [(PPh₃)₃Au₃(μ -BiBzIm)]ClO₄

or in processes in which the displacement proceeds with simultaneous cleavage of the halide bridge (eqns. 6,7)

$$(IV) + \frac{1}{2}Pd_{2}(\mu-Cl)_{2}(C_{6}F_{5})_{2}(tht)_{2}$$

(dppm)Au₂(μ -BiBzIm)Pd(C₆F₅)Cl + tht (6)

$$(IV) + \frac{1}{2}Pd_2(\mu-Cl)_2Cl_2(tht)_2 \rightarrow$$

$$(dppm)Au_2(\mu-BiBzIm)PdCl_2 + tht$$
 (7)

Both types lead to the formation of trinuclear complexes (complex VI-VIII, Table I). Attempts to prepare complex X by displacing the tht group from $Pd(C_6F_5)_2(tht)_2$ proved unsuccessful, and the unchanged reactants were recovered even after 28 h stirring at room temperature.

Addition of NaClO₄ and PPh₃ or AgClO₄ and Tl(acac) allows the synthesis of cationic derivatives (eqns. 8, 9)

 $(dppm)Au_2(\mu-BiBzIm)Pd(C_6F_5)Cl + NaClO_4 + PPh_3 \rightarrow$

 $[(dppm)Au_2(\mu-BiBzIm)Pd(C_6F_5)(PPh_3)]ClO_4 +$

(5)

 $(dppm)Au_2(\mu-BiBzIm)PdCl_2 + AgClO_4 + Tlacac \rightarrow$

$$[(dppm)Au_2(\mu-BiBzIm)Pd(acac)]ClO_4 + AgCl + TlCl (9)$$

The reactions take place smoothly at room temperature, giving rise to the precipitation of \dot{MCl} (M = Na or, respectively Ag and Tl) and to the formation of complexes (XII and XIII, Table I) which can be isolated from the filtrate.

Tetranuclear Complexes

Displacement of the perchlorate group as in (5) (at room temperature in dichloromethane solution, but using a 1:2 ratio of the reactants) according to eqn. (10)

$$(I) + 2 \operatorname{Au}(\operatorname{OClO}_3)\operatorname{PPh}_3 \rightarrow$$

$$[(PPh_3)_4Au_4(\mu-BiBzIm)](ClO_4)_2 \qquad (10)$$

or to eqns. (11) and (12)

(IV) + 2 Au(OClO₃)L →
[(dppm)Au₂(
$$\mu$$
-BiBzIm)Au₂L₂](ClO₄)₂ (11)

 $(IV) + [Au(OClO_3)]_2 dppm \rightarrow$

$$[(dppm)_2Au_4(\mu-BiBzIm)](ClO_4)_2$$
(12)

leads to solutions, which, after partial concentration and addition of ether, render the corresponding tetranuclear complexes (XIV-XVIII, Table I).

Attempts to prepare tetranuclear mixed gold(I)-palladium(II) complexes proved unsuccessful, since the displacement of the perchlorate group proceeds with simultaneous rearrangements (eqns. 13 and 14) leading to the formation of homonuclear compounds.

(I) + 2 Pd(OClO₃)(C₆F₅)(PPh₃)₂
$$\rightarrow$$

2
$$[Au(PPh_3)_2]CIO_4 + Pd_2(\mu-BiBzIm)(C_6F_5)_2(PPh_3)_2$$

(13)

$$(IV) + 2 Pd(OClO_3)(C_6F_5)(PPh_3)_2 \rightarrow$$

 $[Au_2(PPh_3)_2(dppm)](ClO_4)_2 +$

+
$$Pd_2(\mu$$
-BiBzIm)(C₆F₅)₂(PPh₃)₂ (14)

The synthesis of complexes of higher nuclearity is generally hindered by similar rearrangements, which lead to mixtures whose resolution could not be accomplished. Nevertheless, one hexanuclear complex, resulting from the reaction of the acac derivative (XII) with $H_2BiBzIm$ in 2:1 ratio, (eqn. 15), could be isolated

$2[(dppm)Au_2(\mu-BiBzIm)Pd(acac)]ClO_4 + H_2BiBzIm \rightarrow$

 $[{(dppm)Au_2(\mu-BiBzIm)Pd}_2(\mu-BiBzIm)](ClO_4)_2 +$

+ 2 acac (15)

All the complexes are air-stable. Their analytical data, melting points and conductivities, along with the molecular weights of the soluble neutral complexes, are listed in Table I. These data point to three different coordination modes of the $BiBzIm^{2-}$ anion: as bidentate (complexes I-V) (A), as tridentate (complex VI) (B) or as tetradentate ligand (complexes VII-XI) (D) and (complexes XIV-XVIII) (C).

Coordination as tetradentate ligand bridging a larger number of metal atoms, as in F or G, can be ruled out, since a) the molecular weights of the



neutral complexes VIII and X (very low solubility prevents the determination for complexes VII, IX and XI) show they are trinuclear; b) the value of A in Onsager's equation* for complex XII in acetone solutions of different concentrations is 353. This confirms the structure as trinuclear (1:1 electrolyte), since 2:1 electrolytes should give Λ values of *ca*. 600-700 [3].

The IR spectra of the tri- and tetranuclear complexes show absorption bands due to the tetradentate anion BiBzIm²⁻ identical to those described for this ligand in binuclear palladium(II) complexes [3]. The only observed differences are located in the $1300-1200 \text{ cm}^{-1}$ region (in plane C-H bending) where the spectra of complexes I-V and XII-XVIII exhibit a group of four or respectively, two absorption bands.

The pentafluoro and pentachlorophenyl derivatives show absorptions characteristic of these groups [5--7], whereas for complexes VII-IX the bands expected for the metal-halogen vibration (at $350-200 \text{ cm}^{-1}$) are masked by another band, probably arising from the BiBzIm²⁻ anion.

All the cationic complexes exhibit the two absorption bands which are characteristic of the perchlorate anion (Td), at *ca.* 1095(s,br) and 623(s) cm⁻¹.

Experimental

The IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer (over the range $4000-200 \text{ cm}^{-1}$) using Nujol between polyethylene or NaCl sheets. The conductivities were measured in acetone solution with a Philips PW 9501/01 conductimeter. C, H and N analyses were carried out with a Perkin-Elmer 240 microanalyzer. The molecular weights were determined in chloroform solutions with a Hitachi-Perkin-Elmer mod. 115 osmometer. The analytical data, molecular weights and conductivities for the novel compounds are listed in Table I. Au was determined by ashing the samples together with an aqueous solution of hydrazine.

The binuclear palladium compounds were prepared as described elsewhere: $(NBu_4)_2[Pd_2(\mu-Br)_2-(C_6F_5)_4]$ [5], $(NBu_4)_2[Pd_2(\mu-Cl)_2(C_6Cl_5)_4]$ [7], $(NBu_4)_2[Pd_2Br_6]$ [8], $Pd_2(\mu-Cl)_2(C_6F_5)_2(tht)_2$ [9] and $Pd_2Cl_4(tht)_2$ by treating $PdCl_2(tht)_2$ with $PdCl_2$ in refluxing acetone.

The synthesis of $H_2BiBzIm$ was carried out as described in [10].

Preparation of the Complexes

All the reactions were carried out at room temperature.

Binuclear Compounds $[L_2Au_2](\mu$ -BiBzIm)

A solution of AuClL or AuCl₂(L-L) (0.3 mmol) in 20 ml of H₂CCl₂ was stirred with K₂BiBzIm (obtained by treating 0.3 mmol of H₂BiBzIm with 0.6 mmol of KOH in 50 ml of H₂CCl₂/MeOH (1:1) for 0.5 h) for 1-2 h (II, III, V) or, respectively, 24 h (I, IV). The white complexes (IV) and (V) which precipitated spontaneously, were repeatedly washed with H₂O and vacuum-dried (60-80% yield). The white complexes (I) and (II) and the yellow complex (III) were isolated after evaporating the solution to dryness, re-crystallization from dichloromethane and addition of ether to the filtrate (50-70% yield).

Trinuclear Compounds

$\{[(Ph_3P)_3Au_3](\mu-BiBzIm)\}ClO_4(VI)$

An equimolecular mixture (0.25 mmol) of (I) and Au(OClO₃)PPh₃ (obtained *in situ* by reacting AuClPPh₃ with AgClO₄ and subsequent removal of

^{*} $\Lambda_e = \Lambda_o - \Lambda \sqrt{c}$.

AgCl) in 30 ml of H_2CCl_2 was stirred for 2 h. Partial evaporation of the solvent and addition of ether led to the precipitation of the white complex (VI) (75% yield).

$(dppm)Au_2(\mu-BiBzIm)PdX_2$ (X = Cl(VII) or Br (IX))

Complex (IV) (0.28 mmol) was stirred with $PdCl_2(tht)_2$ (0.28 mmol) or $Pd_2(\mu-Cl)_2Cl_2(tht)_2$ (0.14 mmol) in 30 ml of H_2CCl_2 for 16 or, respectively, 3.5 h. The precipitated yellow complex (VII) was filtered off and washed repeatedly with H_2CCl_2 (73% yield).

(IX) was obtained similarly by reacting (IV) with $(Bu_4N)_2[Pd_2(\mu-Br_2Br_4]$. It was washed with methanol (80% yield).

$(dppm)Au_2(\mu-BiBzIm)Pd(C_6F_5)Cl(VIII)$

A mixture of (IV) (0.101 g, 0.10 mmol) and $Pd_2(\mu-Cl)_2(C_6F_5)_2(tht)_2$ (0.04 g, 0.05 mmol) in 50 ml of H_2CCl_2 was stirred for 3.5 h. Partial evaporation of the solvent and addition of methanol led to the precipitation of the white complex (VIII), which was washed with hexane (45% yield).

$(dppm)Au_2(\mu$ -BiBzIm)Pd $(C_6X_5)_2$ (X = F(X) or Cl(XI))

To a H_2CCl_2 solution (30 ml) of $(Bu_4N)_2[Pd_2-(\mu-X')_2(C_6X_5)_4]$ (X = F; X' = Br) (0.08 g, 0.052 mmol) or X = X' = Cl (0.080 g, 0.04 mmol) was added 0.105 g (0.104 mmol) or, respectively, 0.091 g (0.08 mmol) of complex (IV). After 20 h stirring the solution was filtered.

For the pale yellow complex (X) the filtrate was evaporated to dryness and the oily residue was extracted with n-butanol/hexane. For the yellow complex (XI) the filtrate was partially evaporated and butanol was added (X = 56% and XI = 59% yields).

$[(dppm)Au_2(\mu-BiBzIm)Pd(acac)]ClO_4(XII)$

An equimolecular (0.08 mmol) mixture of VII, Tlacac and AgClO₄ in 40 ml of H_2CCl_2 was stirred for 3.5 h in the absence of light. The formed TlCl and AgCl were removed by filtration and the solvent was partially evaporated. Addition of isopropanol led to the precipitation of the orange-yellow complex XII (46% yield).

 $[(dppm)Au_2(\mu-BiBzIm)Pd(C_6F_5)PPh_3]$ ClO₄ (XIII) An equimolecular mixture of (VIII) (0.09 mmol) NaClO₄ and PPh₃ in 30 ml of acetone was stirred for 5 h. The formed NaCl was filtered off and the filtrate was concentrated to dryness. The resulting yellow solid was successively washed with H₂O, isopropanol and ether, filtered, and air-dried (44% yield). Tetranuclear Compounds: $\{[(Ph_3P)_4Au_4](\mu BiBz-Im)\}(ClO_4)_2(XIV)$ and $[(dppm)_2Au_2(\mu BiBzIm)-Au_2L_2](ClO_4)_2(L_2 = dppm(XV); L = PPh_3(XVI), PBu_3^n(XVII) or P(OMe)_3(XVIII))$

To a solution of Au(OClO₃)L or $[Au(OClO₃)]_2$ dppm (0.1 mmol) (obtained *in situ* by reacting AuClL or, respectively, (AuCl)₂dppm with AgClO₄ and removing the formed AgCl) in 50 ml of H₂CCl₂ was added 0.05 mmol of complex (IV). After 15 h stirring, the solution was concentrated to *ca*. 5 ml and ether was added to precipitate complexes XV-XVIII (60-70% yield). (XIV) was similarly obtained by reacting Au(OClO₃)PPh₃ with complex (I) (2:1 ratio) (80% yield).

Preparation of $[{(dppm)Au_2(\mu-BiBzIm)Pd}_2-(\mu-BiBzIm)](ClO_4)_2(XIX)$

A mixture of complex (XII) (0.144 g, 0.1 mmol) and $H_2BiBzIm$ (0.012 g, 0.05 mmol) in 60 ml of acetone was stirred for 86 h. The filtered solution was concentrated to *ca.* 5 ml, and ether was added to precipitate the yellow complex (XIX) (40% yield).

Reaction of $(Ph_3P)_2Au_2(\mu\text{-}BiBzIm)$ with $Pd(OClO_3)-(C_6F_5)(PPh_3)_2$

To a solution of $Pd(OClO_3)(C_6F_5)(PPh_3)_2$ (0.34 mmol) in 40 ml of benzene (obtained in situ by treating $PdCl(C_6F_5)(PPh_3)_2$ with AgClO₄ and filtering off the formed AgCl) was added $[(Ph_3P)_2Au_2]$ -(µ-BiBzIm) (0.2 g, 0.17 mmol). Stirring for 16 h rendered an insoluble solid which was filtered off and extracted with refluxing acetone. The residue was identified by its elemental analysis and IR spectrum $Pd_2(\mu-BiBzIm)(C_6F_5)_2(PPh_3)_2$ [3]. Partial as evaporation of the filtrate and addition of ether yielded a white solid which was identified by IR spectroscopy and elemental analysis as $[Au(PPh_3)_2]$. ClO₄. (Found %: C, 53.5; H, 3.85. Calcd.: C, 52.7; H, 3.65).

Reaction of $(dppm)Au_2(\mu BiBzIm)$ with $Pd(OClO_3)-(C_6F_5)(PPh_3)_2$

To a solution of $Pd(OClO_3)(C_6F_5)(PPh_3)_2$ (0.2 mmol) (obtained as described before) was added $[(dppm)Au_2](\mu$ -BiBzIm) (0.1 g, 0.1 mmol) in 60 ml of H_2CCl_2 and stirred for 20 h. The formed precipitate was identified (elemental analysis, IR spectroscopy) as a mixture of $[Au_2(PPh_3)_2(dppm)](ClO_4)_2$ and $Pd_2(\mu$ -BiBzIm)(C_6F_5)₂(PPh_3)₂, which could not be separated.

References

- 1 R. Usón, J. Vicente and M. T. Chicote, J. Organometal. Chem., 209, 271 (1981).
- 2 R. Usón and J. Gimeno, J. Organometal. Chem., 220, 173 (1981).

- 3 R. Usón, J. Gimeno, J. Forniés and F. Martinez, Inorg. Chim. Acta, 50, 173 (1981).
- 4 R. Usón, J. Gimeno, J. Forniés, F. Martinez and C. Fernandez, Inorg. Chim. Acta, 54, L95 (1981). 5 R. Usón, J. Forniés, F. Martínez and M. Tomás, J.
- Chem. Soc., Dalton, 888 (1980) and references therein.
- 6 J. Casabó, J. M. Coronas and J. Sales, *Inorg. Chim.* Acta, 11, 5 (1974).
- 7 R. Usón, J.Forniés, F. Martínez and M. Tomás, unpublished results.
- C. M. Harris, S. E. Livingstone and M. G. Stephenson, J. Chem. Soc., 3679 (1958).
 R. Usón, J. Forniés, R. Navarro and M. P. Garcia,
- Inorg. Chim. Acta, 33, 69 (1979).
- 10 B. F. Fiselmann, D. N. Hendrickson and G. D. Stucky, *Inorg. Chem.*, 17, 2078 (1978).