Structure of the double salt $[Co^{II}(Cl)L^3]Cl-[Co^{III}(CO_3)L^3]Cl$ $[L^3 = (2R,5R,8R,11R)$-1,7-dibenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane) and related species †

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The hydrochloride of the chiral cyclen ligand L^3 [(2R,5R,8R,11R)-1,7-dibenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane] reacted with $Na_3[Co^{III}(CO_3)_3]$ in acidic and alcoholic aqueous solution to give two crystalline complexes, $[Co^{II}(Cl)L^3]Cl-[Co^{III}(CO_3)L^3]Cl$ and $[Co^{II}(Cl)L^3]Cl$, the crystal structures of which have been determined. The former contains an equimolar mixture of two markedly different crystallographically independent molecules in the unit cell, which have been crystallised independently as two salts variously hydrated. These differ from one another in the oxidation state of the metal, the co-ordination number, and the configurations of asymmetric nitrogens. The molecule $[Co^{II}(Cl)L^3]Cl$ is distorted square pyramidal with the Cl^- ion at the apex and *RRRR* configurations of the four asymmetric N atoms; the carbonato cobalt(III) complex is six-co-ordinated and the N atoms have *RSRS* configurations. The corresponding mixed-valence compound with bromide did not separate, although the analogue of the monomeric carbonate was isolated. The structure determinations of the carbonate and $[Co^{II}(Cl)L^3]Cl$ show that the molecular geometries are essentially the same as those found in the double salt. The formation and stabilisation of the cobalt(II) species is probably due to the steric requirements of the macrocycle.

The optically active cyclen (2R,5R,8R,11R)-1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane $(L^1)^2$ reacts with $Co^{II}Cl_2$ to give only five-co-ordinated $[Co^{II}(Cl)L^1]Cl$ **1** even under oxidative reaction conditions.[3] On the other hand, the reaction of the corresponding non-N-substituted ligand, (2R,5R,8R,11R)-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane $(L^2)^4$ and $Co^{II}Br_2$ in air leads to a *cis*-cobalt(III) complex.[5] The compound, *SSSR-cis*-$[Co^{III}-(H_2O \cdots Br_2)L^2]Br$ **2**[6] is octahedral with folded cyclen. The shape of **2** leaves a space available for the co-ordination of a bidentate ligand such as an amino acid.[7] This series of complexes are rather substitution labile, and the co-ordinated amino acid is released slowly but completely under mild reaction conditions. Therefore, complex **2** is useful for asymmetric synthesis of alanine,[8] and for optical resolution of functionalised amino acids such as serine and threonine.[9] Further, the spin-coupled intermediate formed between **2** and catechol is suggested to be a significant model species in the reaction of native dioxygenase.[10]

These unique properties are assumed to arise from a constraining effect of the macrocycle[11] based on the small size of the 12-membered ring and the presence of four bulky chiral groups. In addition, it seems that the oxidation state of the central cobalt ion and the geometry of the ligand in the series of complexes vary depending on the bulkiness of the substituents at N. In order to clarify this we tried to prepare a chiral cyclen having two symmetrically bound N-benzyl groups, which would correspond to intermediate bulkiness of the substituents at N. Thus the cyclen L^3, (2R,5R,8R,11R)-1,7-dibenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane, was derived from the corresponding compound L^1 by partial debenzylation.[4] It has C_2 symmetry and consists of four repeating head-to-tail units in the ring; the configurations of the four chiral carbon centres are all *R* as are those of L^1 and L^2. The structure of the dihydrobromide of L^3 has previously been determined by X-ray analysis.[12]

L^1 R = R' = CH_2Ph
L^2 R = R' = H
L^3 R = CH_2Ph, R' = H
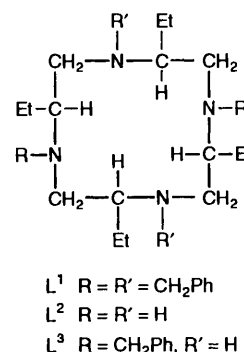
The reaction of L^3 with $Co^{II}X_2$ differs from the cases of L^1 and L^2 in that no product is obtained under various reaction conditions. However, a blue-violet complex was precipitated by the reaction of $L^3 \cdot 3HCl$ with $Na_3[Co^{III}(CO_3)_3]$ in aqueous ethanol solution together with purple crystals. In spite of the fact that a cobalt(III) species was used as the starting material and the reaction was performed in air, an NMR study of both products suggested the presence of paramagnetic species. Accordingly, structure determinations of the complexes obtained under various reaction conditions were carried out by X-ray analysis in order to elucidate their nature.

Experimental

Preparation of compounds

(2R,5R,8R,11R)-1,7-Dibenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane, L^3.[12] The chiral cyclen was prepared by partial debenzylation of L^1 (ref. 2) (8.1 g, 12.6 mmol) in the presence of 10% Pd–C (0.63 g) under H_2 (0.25 mol) in acetic acid (50 cm³) at 22 °C. After removal of the solvent, the mixture was treated with HCl. The hydrochloride obtained was recrystallised from methanol–ethyl acetate (5.3 g, 71%) m.p. 240–245 °C (Found: C, 60.5; H, 9.0; N, 9.9. $C_{30}H_{48}N_4 \cdot 3HCl \cdot H_2O$ requires C, 60.9; H, 9.0; N 9.5%); $[\alpha] -27.1°$ (589 nm,

20.0 g dm^{-3} in MeOH); $\bar{\nu}_{max}$/cm^{-1}(KBr) 719vs, 745vs (Ph). The free base (obtained by treating the HCl salt of L^3 with an excess of alkaline solution): m.p. 116.5–117.5 °C (Found: C, 76.9; H, 10.2; N, 12.0%; M^+, 464. C$_{30}$H$_{48}$N$_4$·0.25H$_2$O requires C, 76.8; H, 10.4; N, 12.0%; M, 464); [α] −93.7° (589 nm, 20.8 g dm^{-3} in MeOH); δ_H(CDCl$_3$) 0.86, 0.93 (12 H, two t, CH$_3$), 1.03 (2 H, m, CH$_3$CH_2 next to PhCH$_2$), 1.15 (2 H, m, CH$_3$CH_2), 1.52 (2 H, m, CH$_3$CH_2), 1.75 (2 H, m, CH$_3$CH_2 next to PhCH$_2$), 2.32–3.85 (18 H, m, CH$_2$, CH, CH$_2$Ph, and NH) and 7.35 (10 H, s, aromatic). The corresponding hydrobromide was obtained from the free base by treatment with HBr (Found: C, 56.5; H, 8.1; N, 8.7. C$_{30}$H$_{48}$N$_4$·2HBr·0.5H$_2$O requires C, 56.7; H, 8.1; N, 8.8%).

$RRRR$-[Co^{II}(Cl)L^3]Cl–$RSRS$-[Co^{III}(Co$_3$)L^3]Cl 3 (= 3a or 3b). This complex was prepared according to a slight modification of the method of Poon and Tobe.[13] The salt Na$_3$[Co^{III}-(CO$_3$)$_3$]·3H$_2$O (506 mg, 1.4 mmol) was added to an ethanol solution (3 cm^3) of L^3·3HCl (770 mg, 1.3 mmol) followed by water (7 cm^3). The resulting mixture was adjusted to pH 3 with dilute HCl, and vigorously stirred and refluxed on a steam-bath for 1 h. The precipitate produced was filtered off and recrystallised from ethanol–ethyl acetate. The filtrate contained a different product which was found to be complex 4 as shown below (Found for 3: C, 59.0; H, 8.0; Cl, 8.6; N, 8.9. C$_{61}$H$_{96}$-Cl$_3$Co$_2$N$_8$O$_3$·1.5H$_2$O requires 59.0; H, 8.0; Cl, 8.6; N, 9.0%); $\bar{\nu}_{max}$/cm^{-1}(KBr) 1635vs (C=O), 745vs and 705vs (Ph). Other physical and spectral data are given in Table 1 together with those of the other complexes.

$RRRR$-[Co^{II}(Cl)L^3]Cl·H$_2$O 4. The filtrate obtained above was condensed nearly to dryness. The residue was purified on a column of SP Sephadex C-25 by elution using 0.5 mol dm^{-3} NaCl. After the eluate had been desalted, a purple solid was recrystallised from ethanol–acetonitrile. At longer reaction time, 4 is obtained as the main product. To an ethanol–water (1:2) solution of L^3·3HCl (945 mg, 1.6 mmol) was added Na$_3$[Co(CO$_3$)$_3$]·3H$_2$O 740 mg (2 mmol). The resulting solution was adjusted to pH 3 with dilute HCl, and refluxed for 2 h. A small amount of complex 5 (see below) was removed by washing with hot water on a filter-paper, and the purple solid recrystallised from ethanol–acetonitrile. During the reaction the formation of acetic acid was recognised by HPLC. Warming of 5 in methanol solution with concentrated HCl[13] also gives 4 (Found: C, 57.7; H, 8.2; Cl, 11.4; N, 8.7. C$_{30}$H$_{50}$Cl$_2$CoN$_4$O·1.5H$_2$O requires 58.0; H, 8.3; Cl, 11.1; N, 9.0%); $\bar{\nu}_{max}$/cm^{-1}-(KBr) 740vs and 718vs (Ph).

$RSRS$-[Co^{III}(CO$_3$)L^3]Cl·2.5H$_2$O 5. To an aqueous solution (100 cm^3) of L^3·3HCl (770 mg, 0.13 mmol) was added Na$_3$[Co(CO$_3$)$_3$]·3H$_2$O (507 mg, 0.15 mmol), and the solution stirred and heated on a steam-bath for 1 h. The resulting violet solution was cooled and filtered. The filtrate was evaporated to dryness and the resulting solid purified on a column of LH-20 eluting with methanol, and recrystallised from acetonitrile–water (224 mg, 26%). In ethanol solution without water, the main product is also 5 (Found: C, 56.1; H, 7.7; N, 8.5. C$_{31}$H$_{48}$ClCoN$_4$O$_3$·2.5H$_2$O requires C, 56.0; H, 8.0; N, 8.4%); $\bar{\nu}_{max}$/cm^{-1}(KBr) 1655vs (C=O), 750s and 702vs (Ph); δ_H(CD$_3$OD) 0.50 (2 H, m, CH$_3$CH_2), 0.64 (6 H, t, CH_3CH$_2$), 1.10 (6 H, t, CH_3'CH$_2$), 1.28 (2 H, m, CH$_3$CH_2), 1.91, 2.15 (4 H, m, m, CH$_3$CH_2'), 2.95 (2 H, dd, CH$_2$), 3.06 (2 H, dd, CH$_2$), 3.18 (2 H, t, CH$_2$'), 3.37 (2 H, m CH$_2$'), 3.33–3.55 (4 H, m, 2NH, 2CH), 3.75 (2 H, m, 2CH'), 3.91 (4 H, ABq, CH$_2$Ph) and 7.44 (10 H, m, aromatic); δ_C(CD$_3$OD) 12.15, 12.72 (CH$_3$, CH$_3$'), 24.24, 25.95 (CH$_3$CH$_2$, CH$_3$CH$_2$'), 52.62, 58.77 (CH$_2$, CH$_2$'), 59.98 (CH$_2$Ph), 66.43, 73.42 (CH, CH'), 130.48, 131.24, 132.86, 133.55 (aromatic) and 170.18 (C=O).

$RSRS$-[Co^{III}(CO$_3$)L^3]Br·2H$_2$O 6. To an aqueous solution (100 cm^3) of L^3·2HBr·0.5H$_2$O (356 mg, 0.56 mmol) was added

Na$_3$[Co(CO$_3$)$_3$]·3H$_2$O (217 mg, 0.60 mmol), and the solution stirred at pH 7.0 and heated on a steam-bath for 1 h. The resulting solution was cooled and filtered. The filtrate was evaporated to dryness. The resulting wine-violet solid was purified on a column of LH-20 eluting with methanol, and recrystallised from acetonitrile–water (246 mg, 63%) (Found: C, 54.8; H, 7.2; Br, 11.7; N, 8.2. C$_{31}$H$_{48}$BrCoN$_4$O$_3$·2H$_2$O requires C, 54.6; H, 7.4; Br, 11.4; N, 8.2%); $\bar{\nu}_{max}$/cm^{-1}(KBr) 1635vs (C=O), 745vs and 705vs (Ph); δ_H(CD$_3$OD) 0.50 (2 H, m, CH$_3$CH_2), 0.66 (6 H, t, CH_3CH$_2$), 1.13 (6 H, t, CH_3'CH$_2$), 1.30 (2 H, m, CH$_3$CH_2), 2.00, 2.18 (4 H, m, m, CH$_3$CH_2'), 2.93 (2 H, dd, CH$_2$), 3.12 (2 H, dd, CH$_2$), 3.23 (2 H, dd, CH$_2$'), 3.37 (2 H, dd, CH$_2$'), 3.33–3.55 (6 H, m, 2NH, 2CH), 3.75 (2 H, m, 2CH'), 3.91 (4 H, ABq, CH$_2$Ph) and 7.44 (10 H, m, aromatic).

Although the corresponding cobalt(II) compound was recognised in the reaction mixture at low pH,[14] no crystalline mixed-valence complexes were observed.

X-Ray data collection and processing for complexes 3, 4 and 6

Since complex 5 gave poor crystals, the bromide complex 6 was used for the X-ray study. The crystal data and experimental conditions are listed in Table 3. The densities of the crystals were obtained by flotation in CCl$_4$–C$_6$H$_6$. A Rigaku AFC-4 four-circle automated diffractometer was employed with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å), and ω (2θ < 30°) and ω–2θ (2θ > 30°) scan modes at a scan rate of 4.0° min^{-1}. Three standard reflections were monitored every 150 for each sample and showed no systematic decrease in intensity.

Structure analysis and refinement. All structures were analysed by direct methods using block-diagonal least-squares refinement (on F) with all non-hydrogen atoms anisotropic and all H atoms isotropic. The H atoms were placed in calculated positions. Unit weights were used for all reflections. The absolute configurations of the complexes were assigned from the known absolute configurations of the macrocycle as an internal reference. The final difference maps showed no peaks higher than 0.9 e Å^{-3} in each case. The programs used and sources of scattering factor data are given in refs. 12 and 15. Calculations were performed on a FACOM M-1800 computer of this Institute. The atomic coordinates are given in Table 4.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Other measurements

Electronic absorption and IR spectra were obtained on Hitachi 330 and Shimazu IR27G spectrophotometers respectively, CD and magnetic circular dichroism (MCD) at 1.08 T on a JASCO J-20A spectropolarimeter. These measurements were made on solutions nearly 1 × 10^{-3} mol dm^{-3}. The ^{1}H NMR spectra were recorded on a JEOL GX-500 (500.0 MHz) spectrometer with SiMe$_4$ in CD$_3$OD as internal reference, and ^{13}C NMR spectra on a JEOL GX-400 (100.4 MHz) spectrometer with dioxane as internal reference. The melting point was measured on a Mettler FP52 apparatus. High-performance liquid chromatography was performed on a JASCO UNIDEC-100-VI instrument.

Results and Discussion

Preparation and characterisation of the complexes

The synthesis was carried out by the method used for the 14-membered tetramine macrocycle 1,4,8,11-tetraazacyclotetradecane (cyclam).[13] With cyclam, a series of complexes cis-[Co^{III}X$_2$(cyclam)]$^+$ (X = Cl, NO$_2$, N$_3$ or NCS) can be derived from the corresponding carbonato complex (X = $\frac{1}{2}$CO$_3$).[13]

Table 1 Spectral and analytical data for the cobalt complexes

Complex	M.p./°C	Visible absorption [a] $\tilde{v}_{max}/10^3$ cm⁻¹ (ε/dm³ mol⁻¹ cm⁻¹)	CD [a] [MCD [a,b]] $\tilde{v}_{ext}/10^3$ cm⁻¹ ($\Delta\varepsilon$/dm³ mol⁻¹ cm⁻¹)
3 [Co^{II}(Cl)L³]Cl–[Co^{III}(CO₃)L³]Cl	233–236	18.02 (464), 26.67 (256)	18.02 (0.3183), 21.05 (−0.8785), 25.19 (0.5730), 28.17 (0.3565) [18.35 (−0.0311), 17.24 (−0.0574)]
4 [Co^{II}(Cl)L³]Cl	248–250	16.95 (40), 18.02 (49), 19.23 (48)	15.50 (0.0216), 18.18 (0.0556), 19.61 (0.0386), 22.47 (−0.0061) [18.35 (−0.0634), 17.24 (−0.1093)]
5 [Co^{III}(CO₃)L³]Cl	222–224	18.18 (398), 26.67 (261)	18.02 (0.2583), 21.05 (−0.8938), 25.32 (0.5535), 28.17 (0.3854)
6 [Co^{III}(CO₃)L³]Br	225–227	18.18 (684), 26.67 (374)	18.02 (0.2473), 21.05 (−0.9654), 25.32 (0.6554), 28.17 (0.4407)

[a] In methanol. [b] At 1.08 T; $\Delta\varepsilon_M$/dm³ mol⁻¹ cm⁻¹ in parentheses.

In the present case, when the reaction was performed in water or in ethanol at neutral pH the cobalt(III) complex *cis*-[Co(CO₃)L³]Cl **5** was obtained exclusively. On the other hand, treatment of L³·3HCl with Na₃[Co^{III}(CO₃)₃] in acidic aqueous ethanolic solution resulted in the mixed-valence complex [Co^{II}(Cl)L³]Cl–[Co^{III}(CO₃)L³]Cl **3** together with [Co^{II}(Cl)L³]Cl **4**. Initially, this result could hardly be explained until the crystal structure revealed the mixed-valence formulation. At room temperature, **5** is stable for a long time in C₂D₅OD or in CD₃OD in a sealed NMR tube. However, prolonged heating at reflux temperature converts it into **4** in acidic aqueous ethanol solution. This means that the product formed at the beginning of the reaction undergoes irreversible reduction by way of acidic hydrolysis in the carbonate system.[16]

There must be a number of factors which contribute to the observed reactivities. The electronic structure, the carbonate-ring strain, the steric requirement of the ligand, the presence of water–ethanol in the acidic medium, *etc.*, may each play some role. The formation of acetic acid tells us that a redox reaction occurs after the ring opening of the carbonate group, where the cobalt(III) complex acts as an oxidising agent and ethanol as a reducing agent. The less-soluble complex **3** first separates from the reaction mixture before undergoing further reduction. If reduction occurs rapidly enough, the product must be a cobalt(II) complex only.

The NMR spectra of complexes **3** and **4** in any solvent showed broadening over a wide range and assignment was impossible even after further purification. This suggests the presence of a high-spin cobalt(II) species.

The visible absorption and CD spectra of complexes **4** and **5** differ significantly from one another as shown in Table 1. For **5** two strong bands in the visible spectrum were observed. This is a typical pattern for a Co^{III}N₅O chromophore,[7,9,17] although **5** is Co^{III}N₄O₂. Both bands split into two component extrema. For **4**, ε and $\Delta\varepsilon$ in the corresponding spectra are about one order of magnitude smaller than those of **5**, and the patterns are more intricate. The tendency towards smaller ε and $\Delta\varepsilon$ values and more complicated patterns is observed in the spectra of the square-pyramidal cobalt(II) complex **1**.[3] The intensities of the two spectra for **3** are nearly equal to the sums of their values for the individual spectra of **4** and **5**. This additivity shows that there is no interaction or transition between the two different cobalt oxidation states in solution. For **3** and **4** the MCD and ESR spectra respectively were observed at 5 K, but **5** and **6** were 'silent'. This demonstrates the validity of the assignment of the valence states in the respective species: *viz.* **3a** and **4** contain paramagnetic Co^{II} and **3b**, **5** and **6** low-spin Co^{III}. The ESR spectral analysis will be reported in detail elsewhere.

Attempts to isolate complex **3** from a mixture of equivalent amounts of **4** and **5** were unsuccessful; **4** usually separated first from various solvents.

Geometries of the complexes

Fig. 1 shows the packing within the unit cell of complex **3**. An unusual aspect of this crystal structure is the presence of two
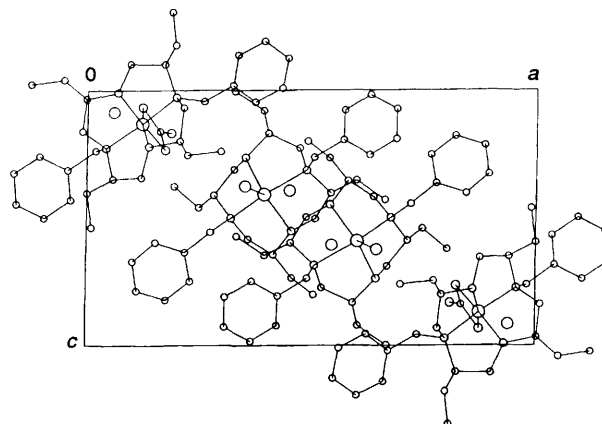
Fig. 1 View of the packing within the unit cell of complex **3** projected along *b*. Hydrogen atoms are omitted for clarity

different, and well separated five- and six-co-ordinated complex molecules **3a** and **3b**. Excluding hydrogen atoms, the intermolecular contacts are all greater than 3.43 Å. The distance between the two cobalt ions Co(A) ··· Co(B) is 6.497(3) Å, and there is no indication of any intermolecular interaction such as association *via* the chloride. Thus, the two independent molecules are just retained favourably in the crystal lattice with only two weak hydrogen bonds, *viz.* Cl(2A) ··· N(10A) ($-x + 1, y + \frac{1}{2}, -z + 1$) 3.26(1) and Cl(B) ··· N(10B) 3.20(1) Å. Fig. 2 shows ORTEP[18] drawings of **3a** and **3b**.

The co-ordination about the Co^{II} in molecule **3a** is square pyramidal with the Cl⁻ ion at the apex, similar to that in complex **1**[3] where the ligand L¹ is the most bulky.[2] The chloride counter ion is at the opposite side of the apical Cl⁻ and approximately on the two-fold axis of the molecule. The chirality of all the asymmetric N atoms is *R* and the configurations are also the same as those reported for **1**. Although the Co–Cl bond distance [2.258(5) Å] in **3a** is very similar to that in **1** [2.258(11) Å], the deviation of the Co from the basal N₄ plane [0.818(6) Å] is fairly larger than that of the latter [0.73(1) Å].[3] The average of the *trans* pair of N–Co–N angles is 135.5(5)° for **3a** and 138.9(11)° for **1**. In view of the relative flexibility, ligand L³ is probably more capable of folding than L¹. The 12-membered ring is square with the asymmetric C atoms at the corners just as in **1**. The same square conformation is also found in the hydrobromide of L³, despite no co-ordination bond.[12]

The six-co-ordinated cobalt(III) molecule **3b** has a distorted geometry with the cyclen co-ordinated to four adjacent positions and the other two *cis* sites occupied by the bidentate carbonate ligand. The counter anion is at the opposite side of the carbonate group, and nearly on the two-fold axis of the molecule. As seen in Table 2, the N–Co–N angles indicate that the cyclen ring adopts the folded form. The configurations at N are *RSRS* so that the strain between the H atoms at N(4) and N(10) and the carbonate group are minimal. The *RSRS* arrangement is also found in the configurational isomer of

Table 2 Bond lengths (Å) and angles (°) around the cobalt ion in complexes 3, 4 and 6

	3a	3b	4	6
Co–Cl(1)	2.258(5)		2.272(3)	
Co···Cl(2)	5.019(5)		4.707(5)	
Co···Cl (or Br)		4.176(5)		5.013(2)
Co–N(1)	2.203(11)	2.020(12)	2.239(9)	2.003(9)
Co–N(4)	2.131(11)	1.940(12)	2.085(9)	1.929(9)
Co–N(7)	2.207(11)	1.988(11)	2.243(9)	2.005(9)
Co–N(10)	2.099(11)	1.917(13)	2.072(10)	1.932(7)
Co–O(1)		1.942(10)		1.910(8)
Co–O(2)		1.932(11)		1.885(6)
Co–Cl(1')			5.380(3)	
Cl(1)–Co–Cl(2)	165.4(1)		88.9(1)	
C(13)···Co···Cl (or Br)		177.1(4)		159.2(3)
Cl(1)–Co–N(1)	109.1(3)		113.3(2)	
Cl(1)–Co–N(4)	101.4(3)		107.2(2)	
Cl(1)–Co–Cl(1')			172.7(3)	
Cl(1)–Co–N(7)	111.5(3)		111.2(2)	
Cl(1)–Co–N(10)	126.4(3)		118.7(3)	
N(1)–Co–N(4)	80.6(4)	83.4(5)	80.1(3)	82.9(4)
N(1)–Co–N(7)	138.3(4)	168.7(5)	135.5(3)	169.4(3)
N(1)–Co–N(10)	81.7(4)	88.1(5)	83.3(4)	89.7(4)
N(4)–Co–N(7)	82.8(4)	88.7(5)	83.3(3)	89.7(4)
N(4)–Co–N(10)	132.2(5)	96.7(5)	134.7(4)	95.2(4)
N(7)–Co–N(10)	81.7(4)	84.8(5)	79.8(3)	83.4(3)
O(1)–Co–O(2)		70.9(4)		69.4(3)
O(1)–Co–N(1)		97.3(4)		97.7(4)
O(1)–Co–N(4)		167.8(5)		165.6(3)
O(1)–Co–N(7)		92.1(5)		91.3(4)
O(1)–Co–N(10)		95.5(5)		99.2(4)
O(2)–Co–N(1)		92.0(4)		90.9(3)
O(2)–Co–N(4)		96.9(4)		96.2(3)
O(2)–Co–N(7)		97.2(4)		97.4(3)
O(2)–Co–N(10)		166.4(5)		168.6(4)

* Symmetry relationship: I − x, y + ½, −z + ½.
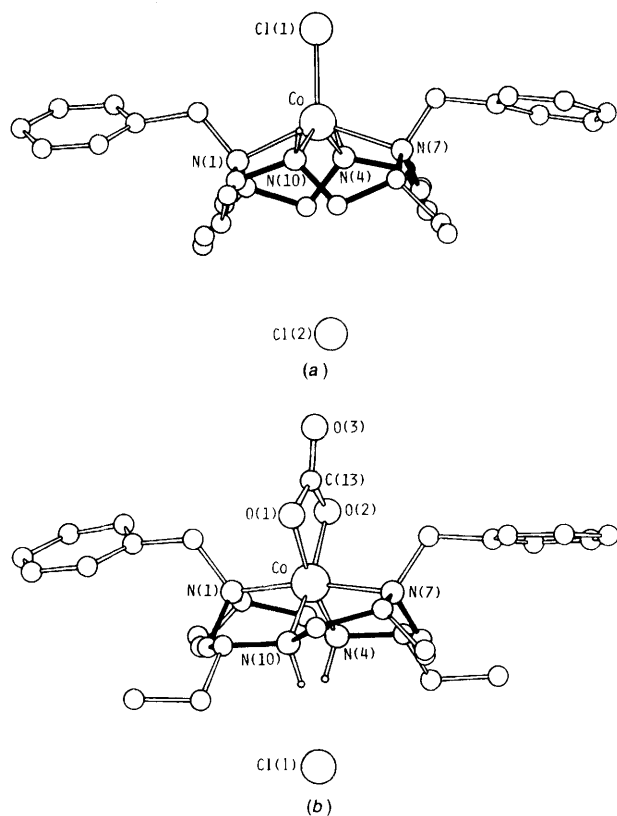
Fig. 2 Molecular structures of (a) complex **3a** and (b) **3b**. Here and in Fig. 3 only the hydrogen atoms at the asymmetric nitrogens are shown for clarity

complex **2**.[15] During the transformation from **5** to **4** in a reaction mixture the configurations at N(4) and N(10) must change from S to R. The mechanism may involve a common deprotonated intermediate for exchange and inversion.[17] Previously we reported on the structure of a carbonato-cobalt(III) complex containing L² as the ligand, which has no benzyl group, and the configurations at N are SSSR.[19] The dimethyl-substituted achiral cyclen 1,7-dimethyl-1,4,7,10-tetraazacyclododecane reacts with Na₃[Co(CO₃)₃] to afford the carbonato-cis-octahedral complex.[20] The exo-exo-exo-endo form[15] for four potentially chiral N atoms in the resulting complex correspond to the SSSR configurations for the case of chiral cyclen. This SSSR type of geometry in either the chiral or achiral cyclen series of complexes appears to be the most preferred when there are two substituted N atoms. On the other hand, the more bulky chiral cyclen may further complicate the situation. Thus the configurations of the nitrogen atoms play an important role in stabilising the various geometries in this series of complexes. The bond parameters of the carbonate moiety approximately agree with those found in related cis-carbonato-cyclen complexes.[19]

The average distance Co^{II}–N is 2.16(1) Å, 0.19 Å longer than the corresponding distance in the cobalt(III) entity [1.97(1) Å]. This difference is comparable to that reported between the hexamine complexes $[Co^{II}(NH_3)_6]^{2+}$ [2.114(9) Å] and $[Co^{III}(NH_3)_6]^{3+}$ [1.935(15) Å], i.e., 0.18 Å.[21] This present series of complexes provides a unique opportunity for comparing bond parameters within the same crystal having the same ligand and counter ion.

Perspective drawings of the molecules **4** (a) and **6** (b) are shown in Fig. 3. When projected on the N₄ mean plane of the 12-membered ring from the side of the respective counter anions the skeleton of the ligands appears to be a distorted square with the chiral groups at the corners. The geometries of the respective molecules are essentially the same as those of **3a**

Table 3 Crystal data and experimental conditions for complexes **3**, **4** and **6**

	3	**4**	**6**
Formula	$C_{61}H_{96}Cl_3Co_2N_8O_3$	$C_{30}H_{50}Cl_2CoN_4O$	$C_{31}H_{52}BrCoN_4O_5$
M	1213.693	612.586	699.614
Colour	Blue-violet	Purple	Wine-violet
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1$	$P2_12_12_1$	$P2_1$
$a/\text{Å}$	19.922(9)	20.833(8)	14.998(9)
$b/\text{Å}$	13.908(4)	15.253(4)	14.757(5)
$c/\text{Å}$	11.414(4)	10.033(2)	14.323(4)
$\beta/°$	91.56(3)		103.37(3)
$U/\text{Å}^3$	3161(2)	3188(2)	1661(1)
Z	2	4	2
$D_m/\text{Mg m}^{-3}$	1.275	1.274	1.394
$D_c/\text{Mg m}^{-3}$	1.272	1.276	1.395
$F(000)$	1294	1308	716
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	6.98	7.33	1.75
Crystal dimensions/mm	$0.38 \times 0.30 \times 0.25$	$0.42 \times 0.42 \times 0.45$	$0.40 \times 0.40 \times 0.15$
No. observed reflections [a]	6708	2446	3186
No. unique reflections	3002	2321	2965
No. unobserved reflections	4921	1769	1343
No. variables	1079	536	568
R [b]	0.057	0.067	0.069
R' [c]	0.060	0.066	0.072
Δ/σ in final cycle	0.20	0.16	0.28
$\rho_{max}/\text{e Å}^{-3}$	0.42	0.51	0.85 [d]

[a] Criterion: $|F_o| > 3\sigma(|F_o|)$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [d] There is one high ghost peak near Br^-

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Table 4 Atomic coordinates ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
(*a*) Complex **3**							
Co(A)	3963(1)	0	4080(2)	Co(B)	1235(1)	1358(2)	1302(2)
Cl(1A)	3535(2)	1483(3)	3755(4)	Cl(B)	597(2)	4196(3)	845(6)
Cl(2A)	4526(2)	−3514(3)	3931(4)	O(1B)	1758(5)	524(7)	2343(10)
N(1A)	3221(6)	−874(8)	5002(9)	O(2B)	1236(4)	72(8)	660(8)
C(2A)	2843(7)	−1470(11)	4109(13)	C(13B)	1641(8)	−195(10)	1606(14)
C(3A)	3291(7)	−1705(9)	3098(13)	O(3B)	1890(6)	−996(8)	1675(11)
N(4A)	3541(6)	−777(9)	2629(10)	N(1B)	1994(6)	1772(8)	277(10)
C(5A)	4048(7)	−852(10)	1686(11)	C(2B)	1721(8)	1732(11)	−1029(13)
C(6A)	4740(7)	−982(10)	2262(13)	C(3B)	946(8)	1645(12)	−1049(14)
N(7A)	4904(5)	−216(7)	3140(.9)	N(4B)	678(6)	1941(8)	77(10)
C(8A)	5443(7)	−532(9)	4028(13)	C(5B)	−33(8)	1636(10)	331(13)
C(9A)	5100(7)	−1070(10)	5030(14)	C(6B)	−113(7)	1811(11)	1609(15)
N(10A)	4576(5)	−424(8)	5513(10)	N(7B)	421(5)	1211(8)	2255(10)
C(11A)	4178(7)	−883(10)	6439(12)	C(8B)	587(7)	1642(11)	3479(14)
C(12A)	3615(8)	−1483(10)	5826(12)	C(9B)	1224(8)	2248(13)	3425(15)
C(21A)	2513(9)	−2415(12)	4587(14)	N(10B)	1384(6)	2505(9)	2203(11)
C(22A)	1965(12)	−2766(17)	3764(21)	C(11B)	2084(7)	2807(11)	1996(14)
C(51A)	3935(8)	−1619(12)	789(14)	C(12B)	2163(7)	2751(10)	682(13)
C(52A)	3288(10)	−1436(12)	28(14)	C(21B)	1959(9)	2553(13)	−1783(16)
C(81A)	6011(8)	−1139(11)	3532(15)	C(22B)	1873(9)	2236(13)	−3076(16)
C(82A)	6643(9)	−1106(16)	4291(17)	C(51B)	−543(8)	2217(13)	−434(16)
C(111A)	4594(9)	−1481(11)	7344(13)	C(52B)	−1260(10)	1843(15)	−263(18)
C(112A)	5080(9)	−824(12)	7999(14)	C(81B)	−2(9)	2214(12)	4031(14)
C(11aA)	2778(7)	−158(11)	5548(13)	C(82B)	110(10)	2282(15)	5368(17)
C(12aA)	2218(8)	−498(11)	6343(13)	C(111B)	2256(9)	3791(13)	2541(16)
C(13aA)	2342(7)	−802(12)	7467(14)	C(112B)	2990(10)	4099(15)	2394(18)
C(14aA)	1799(8)	−1024(12)	8195(14)	C(11aB)	2611(6)	1132(9)	429(14)
C(15aA)	1142(10)	−883(14)	7839(17)	C(12aB)	3247(6)	1441(12)	−198(13)
C(16aA)	1046(8)	−593(14)	6701(17)	C(13aB)	3337(7)	1243(12)	−1396(13)
C(17aA)	1552(8)	−399(13)	5956(16)	C(14aB)	3926(7)	1466(12)	−1936(14)
C(71A)	5068(7)	724(9)	2628(14)	C(15aB)	4450(8)	1869(11)	−1270(13)
C(72A)	5715(7)	807(10)	1952(13)	C(16aB)	4339(8)	2046(12)	−95(15)
C(73A)	6291(8)	1134(10)	2529(15)	C(17aB)	3742(7)	1869(11)	459(14)
C(74A)	6889(9)	1222(14)	1912(19)	C(71B)	192(7)	178(11)	2376(14)
C(75A)	6892(11)	986(14)	736(21)	C(72B)	−429(7)	36(13)	3124(14)
C(76A)	6302(11)	640(15)	178(17)	C(73B)	−1053(8)	15(14)	2574(17)
C(77A)	5732(8)	592(13)	786(14)	C(74B)	−1620(8)	−93(16)	3221(18)
				C(75B)	−1570(8)	−142(14)	4432(17)
				C(76B)	−947(9)	−152(15)	4985(16)
(*b*) Complex **4**				C(77B)	−368(8)	−99(14)	4291(15)
Co	111(1)	633(1)	2531(2)				
Cl(1)	61(2)	−848(2)	2341(4)	C(81)	−922(5)	2456(8)	5211(11)
Cl(2)	396(2)	300(3)	7158(4)	C(82)	−798(7)	2764(9)	6627(14)
N(1)	944(4)	1222(5)	1449(8)	C(111)	1624(5)	1831(8)	4911(11)
				C(112)	2339(5)	1772(8)	4725(12)

Table 4 (*continued*)

| Atom	x	y	z	Atom	x	y	z
C(2)	687(5)	1733(7)	277(9)	C(11a)	1344(5)	463(6)	996(10)
C(3)	−11(4)	1972(6)	536(9)	C(12a)	1988(5)	697(7)	308(10)
N(4)	−358(4)	1158(5)	888(8)	C(13a)	2024(6)	793(8)	−1049(12)
C(5)	−1046(4)	1291(6)	1248(10)	C(14a)	2619(7)	971(8)	−1643(12)
C(6)	−1080(4)	1703(6)	2632(12)	C(15a)	3169(6)	1003(7)	−873(14)
N(7)	−740(4)	1159(5)	3635(8)	C(16a)	3142(6)	881(8)	465(14)
C(8)	−500(5)	1669(7)	4806(10)	C(17a)	2545(5)	735(7)	1057(11)
C(9)	202(4)	1955(6)	4537(10)	C(71)	−1130(5)	385(7)	4065(12)
N(10)	560(4)	1168(5)	4187(9)	C(72)	−1733(5)	581(7)	4814(12)
C(11)	1247(5)	1323(7)	3835(11)	C(73)	−2305(5)	705(7)	4149(11)
C(12)	1277(4)	1765(6)	2452(12)	C(74)	−2873(7)	890(8)	4814(12)
C(21)	1074(6)	2567(8)	−70(13)	C(75)	−2873(7)	953(10)	6166(17)
C(22)	924(7)	2918(11)	−1476(14)	C(76)	−2313(8)	824(9)	6883(14)
C(51)	−1425(5)	1767(8)	192(12)	C(77)	−1731(7)	608(9)	6218(12)
C(52)	−2157(6)	1710(8)	419(13)	O(w)	−522(4)	−507(7)	9283(10)
(b) Complex 6							
Co	3197(1)	0	2834(2)	C(52)	2179(9)	−3496(19)	5730(10)
Br	694(2)	−3731(3)	1487(6)	C(81)	481(7)	644(14)	2545(8)
O(1)	3334(6)	2178(6)	2523(6)	C(82)	−198(8)	1759(17)	1867(11)
O(2)	4050(4)	955(9)	3932(5)	C(111)	2231(8)	−1414(17)	−338(8)
C(13)	3930(7)	2323(14)	3464(9)	C(112)	2691(11)	−1319(22)	−1254(10)
O(3)	4248(7)	3566(12)	3818(8)	C(11a)	4716(7)	431(14)	1871(9)
N(1)	4141(5)	−863(10)	2167(6)	C(12a)	5462(7)	−135(17)	1402(9)
C(2)	4695(6)	−1989(13)	2963(8)	C(13a)	6288(8)	−398(17)	2049(10)
C(3)	4205(7)	−2443(13)	3843(8)	C(14a)	7000(9)	−887(23)	1638(12)
N(4)	3269(5)	−2067(10)	3477(6)	C(15a)	6860(10)	−1111(18)	540(14)
C(5)	2758(7)	−1980(13)	4339(8)	C(16a)	6075(10)	−846(19)	−119(9)
C(6)	1929(7)	−1103(12)	3821(8)	C(17a)	5361(8)	−333(9)	300(9)
N(7)	2142(5)	481(10)	3423(6)	C(71)	2348(7)	1684(13)	4324(8)
C(8)	1425(7)	1097(15)	2490(8)	C(72)	1639(7)	1921(13)	4950(8)
C(9)	1623(7)	631(16)	1425(8)	C(73)	983(8)	3019(16)	4657(10)
N(10)	2320(5)	−576(11)	1568(6)	C(74)	361(9)	3246(19)	5262(12)
C(11)	2815(7)	−711(14)	702(7)	C(75)	417(9)	2352(20)	6179(11)
C(12)	3624(7)	−1650(14)	1178(8)	C(76)	1074(8)	1307(21)	6497(10)
C(21)	5007(7)	−3455(15)	2455(8)	C(77)	1695(8)	1074(17)	5889(9)
C(22)	5797(9)	−4188(17)	3202(10)	O(w1)	1082(8)	−6559(16)	−348(10)
C(51)	2596(9)	−3608(17)	4761(9)	O(w2)	2708(6)	−4770(11)	2044(7)
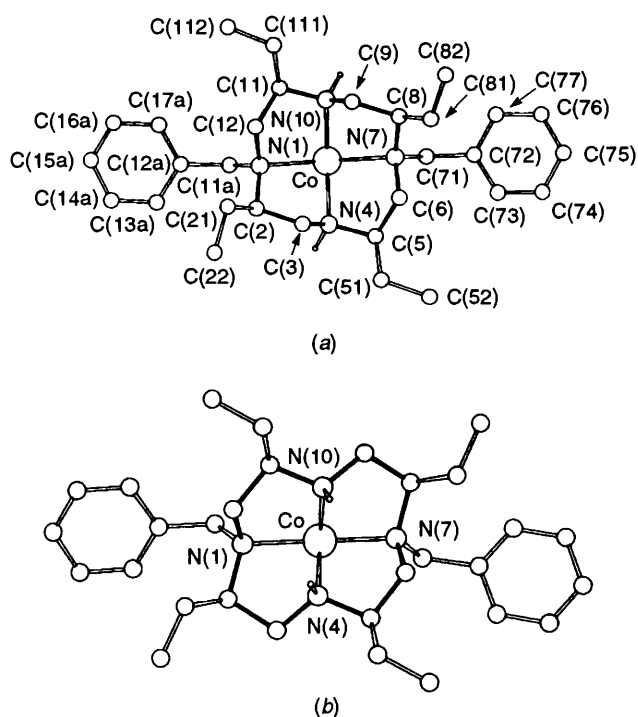
Fig. 3 Views of the cations of complexes 4 (*a*) and 6 (*b*)

and **3b** respectively. No particularly abnormal values in bond parameters are found in all the new compounds compared

with other related complexes. Unlike **3**, the respective counter anions are not present on the two-fold axis but in the appropriate space. In **4** the deviation of Co from the basal N_4 plane [0.829(5) Å] is comparable to that found in **3a**. Both metal and Cl(1) ions are situated approximately on the crystallographic two-fold axis, and are aligned along this axis where the apical Cl(1) of the next molecule (symmetry $-x$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$) is situated instead of the counter ion Cl(2). The distance between Co and the apical Cl(1) ions of the next unit is 5.380(3) Å and the angle Cl(1)–Co ··· Cl(1) is 172.7(3)°. The hydrogen-bond distances between the water molecules and Cl(2) or N(4) ($x + 1$, $y, z − 1$) are 3.12(1) and 3.03(1) Å respectively. Three hydrogen bonds are also observed in **6**: Br ··· O(w1) ($-x$, $y + \frac{1}{2}$, $-z$) 3.37(1), Br ··· O(w2) ($x, y + 1, z$) 3.182 (9) and O(1) ··· O(w2) ($x, y + 1, z$) 2.78 (1) Å.

Conclusion

The structure determination and the other spectral data on complex **3** showed that the crystal contains simultaneously two different valence states of cobalt, two co-ordination numbers, and two different stereochemistries. The formation of cobalt(ii) species from the cobalt(iii) complex first produced is explained on the basis of the steric requirements of the ligand including the constraining effect of the macrocycle.

Whereas the cyclen L^2 reacts with the cobalt(ii) salt to afford exclusively a cobalt(iii) product in the air,[5] the dibenzylcyclen L^3 gave both cobalt-(ii) and -(iii) species. For the tetrabenzyl-cyclen L^1 the planar conformation is preferred in a complex for steric reasons. On the other hand, the favoured form of

the non-N-substituted cyclen L^2 is folded as in the case of cyclam.[13] For L^3, both planar and folded geometries are possible depending on the circumstances, and the former appears to be preferred. When the carbonato cobalt(III) source is used as the starting reagent L^3 gives first the six-co-ordinated octahedral complex **3b** or **5** where the carbonate group remains unchanged. After opening of the carbonate four-membered ring under acidic conditions, the molecule changes irreversibly to a planar five-co-ordinate cobalt(II) complex due to the steric requirements. The formation of the crystalline double salt **3** presumably depends on a delicate balance of packing forces.

According to the classification of mixed-valence complexes proposed by Robin and Day,[22] **3** belongs to class I; the different cobalt oxidation states exist independently without interaction in the crystal and its properties are equal to those of the sum of the individual parts. Although mixed-valence complexes are by no means uncommon, few examples are known for this type of cobalt complex.[23]

References

1 Part 15, N. Azuma, Y. Kohno, F. Nemoto, Y. Kajikawa, K. Ishizu, T. Takakuwa, S. Tsuboyama, K. Tsuboyama, K. Kobayashi and T. Sakurai, *Inorg. Chim. Acta*, 1994, **215**, 109.
2 S. Tsuboyama, K. Tsuboyama, I. Higashi and M. Yanagita, *Tetrahedron Lett.*, 1970, 1367; T. Sakurai, K. Kobayashi, T. Kanari, T. Kawata, I. Higashi, S. Tsuboyama and K. Tsuboyama, *Acta Crystallogr., Sect. B*, 1983, **39**, 84.
3 T. Sakurai, K. Kobayashi, A. Hasegawa, S. Tsuboyama and K. Tsuboyama, *Acta Crystallogr., Sect. B*, 1982, **38**, 107.
4 K. Tsuboyama, S. Tsuboyama, J. Uzawa, K. Kobayashi and T. Sakurai, *Tetrahedron Lett.*, 1977, 4603.
5 S. Tsuboyama, K. Tsuboyama, T. Sakurai and J. Uzawa, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 267.
6 T. Sakurai, S. Tsuboyama and K. Tsuboyama, *Acta Crystallogr., Sect. B*, 1980, **36**, 1797.
7 S. Tsuboyama, T. Sakurai and K. Tsuboyama, *J. Chem. Soc., Dalton Trans.*, 1987, 721.
8 S. Tsuboyama, T. Takishima, T. Sakurai and K. Tsuboyama, *Nippon Kagaku Kaishi*, 1987, 313.
9 S. Tsuboyama, S. Miki, T. Chijimatsu, K. Tsuboyama and T. Sakurai, *J. Chem. Soc., Dalton Trans.*, 1989, 2359.
10 S. Nakashima, H. Ohya-Nishiguchi, N. Hirota, S. Tsuboyama and T. Chijimatsu, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1225.
11 F. L. Urbach, in *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Melson, Plenum, New York, London, 1979, p. 345.
12 K. Kobayashi, S. Tsuboyama, K. Tsuboyama and T. Sakurai, *Acta Crystallogr., Sect. C*, 1994, **50**, 307.
13 C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 1968, 1549.
14 S. Tsuboyama and K. Tsuboyama, unpublished work.
15 S. Tsuboyama, Y. Shiga, Y. Takasyo, T. Chijimatsu, K. Kobayashi, K. Tsuboyama and T. Sakurai, *J. Chem. Soc., Dalton Trans.*, 1992, 1783.
16 J. F. Endicott, N. A. P. Kane-Maguire, D. P. Rillema and T. Roch, *Inorg. Chem.*, 1973, **12**, 1818.
17 D. A. Buckingham, P. J. Cresswell, R. J. Dellaca, M. Dwyer, G. J. Gainsford, L. G. Marzilli, I. E. Maxwell, W. T. Robinson, A. M. Sargeson and K. R. Turnbull, *J. Am. Chem. Soc.*, 1974, **96**, 1713.
18 C. K. Johnson, ORTEP, Report ORNL 5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
19 S. Tsuboyama, S. Miki, K. Kobayashi, K. Tsuboyama and T. Sakurai, *Acta Crystallogr., Sect. C*, 1989, **45**, 1621.
20 J. Giusti, S. Chamichi, M. Ciampolini, M. Sabat and D. Masi, *Inorg. Chim. Acta*, 1984, **88**, 51.
21 N. E. Kime and J. A. Ibers, *Acta Crystallogr., Sect. B*, 1969, **25**, 168; H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 2304.
22 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247; G. C. Allen and N. S. Hash, *Prog. Inorg. Chem.*, 1967, **8**, 357.
23 D. W. Meek, E. C. Alyea, J. K. Stralick and J. A. Ibers, *J. Am. Chem. Soc.*, 1969, **91**, 4920; *Inorg. Chem.*, 1970, **9**, 453; J. Ochocki, P. H. Chaudhuri, W. L. Driessen, R. A. G. De Graaf, F. B. Hulsbergen and J. Reedijk, *Inorg. Chim. Acta*, 1990, **167**, 15.