# Preparation and characterization of tetrachlorocobaltates(II) of α,ω-alkylenediammonium. Magnetic and thermal properties. Crystal structure of [NH₃(CH₂)₅NH₃]CoCl₄

J. J. Criado,[a] A. Jiménez-Sánchez,[b] F. H. Cano,[c] R. Sáez-Puche[d] and E. Rodríguez-Fernández[a]*

[a]*Departamento de Química Inorgánica, Plaza de la Merced s/n, E-37008 Salamanca, Spain,* [b]*Departamento de Química Orgánica, Plaza de la Merced s/n, E-37008 Salamanca, Spain,* [c]*Instituto de Quimico-Fisica, Rocasolano CSIC, Departamento de Cristalografia, Serrano 119, E-28006 Madrid, Spain, and* [d]*Departamento de Química Inorgánica, Universidad Complutense, E-28002 Madrid, Spain. E-mail: erodri@gugu.usal.es*

## Abstract

Tetrachlorocobaltates(II) of diprotonated α,ω-diaminoalkanes with the formula [NH₃(CH₂)ₙNH₃]CoCl₄, where $n = 5$ (cadaverine; 1,5-pentanediammonium tetrachlorocobaltate), 8 (1,8-octanediammonium tetrachlorocobaltate) and 10 (1,10-decanediammonium tetrachlorocobaltate), were prepared. The compounds were studied by mass spectrometry, FT-IR and visible spectroscopy, magnetic susceptibility techniques and thermal analysis. The compounds contain the tetrahedral tetrachlorocobaltate(II) ion and the corresponding diprotonated diamine (cadaverine, 1,8-octamethylenediamine and 1,10-decamethylenediamine). The compound corresponding to cadaverine crystallizes in the monoclinic space group $P2_1/c$, with lattice parameters $a = 7.1633\,(7)$, $b = 15.940\,(3)$, $c = 11.137\,(2)$ Å, $\beta = 98.44\,(1)°$ and $Z = 4$. Its crystal structure contains slightly distorted tetrahedral $CoCl_4^{2-}$ ions: the largest difference in Co—Cl bond lengths is 0.029 Å and the largest difference in Cl—Co—Cl angles is 7.76°. The compound also contains diprotonated cadaverine ions. An extensive hydrogen-bonding network connects these ions. The slightly positive deviations of the magnetic susceptibility from the Curie–Weiss law are in agreement with the $^4A_2$ ground state for the tetrachlorocobaltate anion. The compounds with eight and ten C atoms show phase transitions in the solid state and a greater complexity is observed in their differential scanning calorimetry curves. Unfortunately, no suitable single crystals of these could be obtained.

## 1. Introduction

The tetrachlorocobaltate(II) ion has a tetrahedral geometry, although this may be distorted to $D_{2d}$ symmetry. The distortion is evident from a splitting of the bands in the visible and IR spectra (Marcotrigiano *et al.*, 1976, 1977).

Compounds of tetrahedral cobalt(II) have been of continuing interest during the last two decades for several reasons (Morón *et al.*, 1991). In a tetrahedral environment the ground state of cobalt(II) will be $^4A_2$ and axial distortions will split this state into two Kramers doublets. Most energy studies on tetrahedral cobalt(II) compounds reveal two characteristics in common: the first is the relatively large zero-field splitting effect (ZSE; Carlin, 1981, 1985) and the second is that the magnetic exchange in tetrahedral cobalt(II) compounds for most of the compounds investigated is found to be ordered at temperatures below 1 K (Carlin, 1986). Recently, however, new tetrahedral cobalt(II) compounds have been reported showing ferro- or antiferromagnetic interactions, with critical temperatures above 4.2 K, and even as high as 10 K in the case of $Na_2CoP_2O_7$ (Sanz *et al.*, 1999; Chen *et al.*, 1994). This



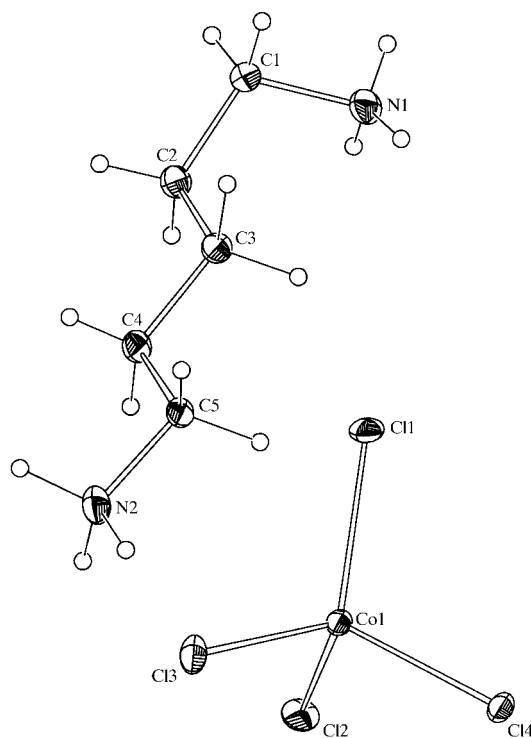Fig. 1. Displacement ellipsoid plot of [NH₃(CH₂)₅NH₃]CoCl₄ with the atom-labelling scheme. H atoms have been assigned arbitrary radii for clarity.

work reports on the magnetic behaviour of different tetrahedral cobalt(II) compounds.

Some diamines, such as 1,4-diaminobutane (putrescine) or 1,5-diaminopentane (cadaverine), have important biological functions in living beings, in which they mainly exist as diprotonated species (Ganem, 1982). If the hydrocarbon chain is sufficiently long, the $[NH_3(CH_2)_nNH_3]^{2+}$ cation will have lipid-like properties. The ammonium groups are held in place by hydrogen-bonding to the Cl atoms of $[CoCl_4]^{2-}$. The thermal behaviour of these compounds shows chain-melting transitions, defined by rapid motion of one or more *gauche* bonds up and down the hydrocarbon chains. The minor transitions are associated with dynamic rotational disordering of the chains. These compounds provide the basis for developing systems which combine bilayer characteristics within a crystalline lattice (Needham *et al.*, 1984).

## 2. Experimental

The CoCl$_2$.6H$_2$O and the highly purified diamines used were obtained from Fluka. The title compounds were prepared in accordance with a previously proposed method (Bañares *et al.*, 1984) and were recrystallized from aqueous solutions. The cobalt content was determined by complexometric titration using edta and murexide as an indicator. The chloride content was determined by the Mohr method (Bañares *et al.*, 1984). A Perkin–Elmer 2400 analyzer was used to determine the carbon, nitrogen and hydrogen present.

$[NH_3(CH_2)_5NH_3]CoCl_4$, cadaverine compound. Found: N, 9.3; C, 19.6; H, 5.3; Cl, 46.2; Co, 19.2%. C$_5$H$_{16}$Cl$_4$CoN$_2$ requires N, 9.19; C, 19.69; H, 5.29; Cl, 46.50; Co, 19.33%. FT-IR (cm$^{-1}$): 3165s, 3120s, 3080sh, 2920s, 2840s, 1575s, 1490s, 1070m, 1050m, 1030m, 760m, 280m. MS-FAB+ ($z/m$): 268.0 $[M-HCl]^+$.

$[NH_3(CH_2)_8NH_3]CoCl_4$, 1,8-octamethylenediamine compound. Found: N, 8.2; C, 27.6; H, 6.3; Cl, 41.5; Co, 16.8%. C$_8$H$_{22}$Cl$_4$CoN$_2$ requires N, 8.07; C, 27.69; H, 6.39; Cl, 40.87; Co, 16.98%. FT-IR (cm$^{-1}$): 3180sh, 3120s, 3060sh, 2920s, 2840s, 1590s, 1565m, 1470s, 1090m, 1060m, 1040m, 810m, 760m, 295m, 285sh. MS-FAB+ ($z/m$): 310.0 $[M-HCl]^+$.

$[NH_3(CH_2)_{10}NH_3]CoCl_4$, 1,10-decamethylenediamine compound. Found: N, 7.5; C, 32.0; H, 6.7; Cl, 37.5; Co, 15.8%. C$_5$H$_{26}$Cl$_4$CoN$_2$ requires N, 7.47; C, 32.02; H, 6.99; Cl, 37.81; Co, 15.71%. FT-IR (cm$^{-1}$): 3180sh, 3120s, 3040sh, 2920s, 2840s, 1590s, 1560m, 1480m, 1070m, 1050m, 1030m, 830m, 810m, 290(broad). MS-FAB+ ($z/m$): 338.1 $[M-HCl]^+$.

The thermal decomposition of the different samples was monitored by thermogravimetric analysis (TGA), using a Perkin–Elmer TGS-2 thermobalance, and by differential scanning calorimetry (DSC) on a Perkin–Elmer DSC-4 apparatus. Sample masses for thermal studies were 5–7 mg. IR spectra were recorded on a Perkin–Elmer 1700 instrument using KBr pellets or Nujol mulls on a CsI window (for the far-IR region). X-ray powder data were obtained on a Siemens D500 diffractometer using nickel-filtered Cu $K\alpha$ radiation. X-ray diffraction data were collected at room temperature on a four-circle Seifert XRD 3000 diffractometer using Cu $K\alpha$ radiation ($\lambda$ = 1.5418 Å), a graphite monochromator and $\omega$–2$\theta$ scans. The lattice parameters were refined from 54 reflections (2 < $\theta$ < 35°). Crystal data and selected details of the structure determinations are given in Table 1. The structure was solved by direct methods (*SIR*92; Altomare *et al.*, 1994) and refined with anisotropic displacement parameters for non-H atoms and isotropic displacement parameters for H atoms
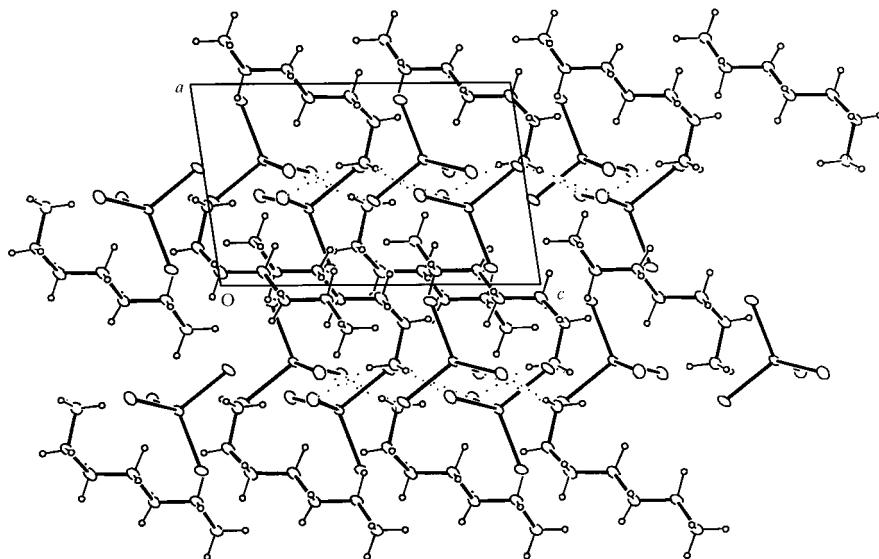


Fig. 2. Projection along the *b* axis of $[NH_3(CH_2)_5NH_3]CoCl_4$, showing a two-dimensional network structure formed by hydrogen bonds.

[*XRAY80* (Stewart *et al.*, 1990), *SHELXL*93 (Sheldrick, 1993)]. Empirical absorption corrections (range 0.073–0.203) were applied using *DIFABS* (Walker & Stuart, 1983). H atoms were located using the program *HSEARCH* (Fallos & Martinez-Ripoll, 1990) and refined with isotropic displacement parameters. The complete lists of atomic coordinates, and bond lengths and angles have been deposited as supplementary material.†

Magnetic susceptibility measurements were performed on a Squid Quantum Design XL magnetometer at 500 Oe in the 300–2 K temperature range. The instrument was calibrated with metallic palladium as standard and all data were corrected for ionic diamagnetism (Mulay & Boudreaux, 1976).

## 3. Crystal structure

The crystal structure of the cadaverine compound shows the tetrachlorocobaltate anion with only slight deviations from a tetrahedron, in agreement with the unsplit Co—Cl stretching band. The tetrahedra are interconnected *via* hydrogen bonds to diprotonated cadaverine. The C—C and C—N bonds in the $C_5H_{16}N_2^{2+}$ cation are similar in length to the same bonds in $[C_5H_{16}N_2]_2Cl_2[PtCl_6]$ (Delafontaine *et al.*, 1987). There are four possible hydrogen bonds, ranging from ammonium to Cl atoms (Table 2). Consideration of H···Cl distances allows the hydrogen bonds to be classified as medium to very weak (see Figs. 1 and 2, and Tables 1 and 3). In our compound with cadaverine, the largest difference in Co—Cl bond lengths is 0.029 Å and the largest difference in Cl—Co—Cl angles is 7.76°, indicating a small distortion from ideal tetrahedral symmetry. These values are similar to those determined for the compound with 1,3-propanodiamine: 0.024 Å and 6.3°, respectively (Ning *et al.*, 1992). The tetrachlorocobaltate(II) ion is found to have a fairly undistorted tetrahedral geometry in $[NH_2(CH_3)_2]_2CoCl_4$ (Williams *et al.*, 1992) and $[N(CH_3)_4]_2CoCl_4$ (Wiesner *et al.*, 1964). For the compound with ethylenediamine, the differences are 0.041 Å and 23.0°, respectively (Smith & Stratton, 1977). No studies on crystal structures of the compounds with eight and ten C atoms were carried out because it was not possible to crystallize them.

## 4. Results and discussion

The IR spectra were consistent with the diprotonated diamine. The Co—Cl stretching vibration appears close to 300 cm$^{-1}$ for tetrahedral $CoCl_4^{2-}$ (Sabatini & Sacconi, 1964). A loss of symmetry leads to a more or less pronounced splitting in this band, as in ethylene-

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† Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM0020). Services for accessing these data are described at the back of the journal.

## Table 1. *Experimental details*

| | |
|---|---|
| **Crystal data** | |
| Chemical formula | $[(NH_3)_2C_5H_{10}].CoCl_4$ |
| Chemical formula weight | 304.93 |
| Cell setting | Monoclinic |
| Space group | $P2_1/c$ |
| $a$ (Å) | 7.1633 (7) |
| $b$ (Å) | 15.940 (3) |
| $c$ (Å) | 11.137 (2) |
| $\beta$ (°) | 98.44 (1) |
| $V$ (Å$^3$) | 1257.9 (3) |
| $Z$ | 4 |
| $D_x$ (Mg m$^{-3}$) | 1.610 |
| Radiation type | Cu $K\alpha$ |
| Wavelength (Å) | 1.5418 |
| No. of reflections for cell parameters | 54 |
| $\theta$ range (°) | 4.88–66.12 |
| $\mu$ (mm$^{-1}$) | 18.178 |
| Temperature (K) | 293 (2) |
| $F(000)$ | 620 |
| Crystal form | Rectangular |
| Crystal size (mm) | $0.47 \times 0.27 \times 0.13$ |
| Crystal colour | Blue |
| | |
| **Data collection** | |
| Diffractometer | Seifert XRD 3000 four-circle |
| Data collection method | $2\theta$–$\omega$ scans |
| $T_{min}$ | 0.073 |
| $T_{max}$ | 0.203 |
| No. of measured reflections | 2147 |
| No. of independent reflections | 2147 |
| No. of observed reflections | 1586 |
| Criterion for observed reflections | $I > 2\sigma(I)$ |
| $\theta_{max}$ (°) | 66.12 |
| Range of $h, k, l$ | $-8 \rightarrow h \rightarrow 8$ |
| | $0 \rightarrow k \rightarrow 19$ |
| | $0 \rightarrow l \rightarrow 13$ |
| No. of standard reflections | 2 |
| Intensity decay (%) | Negligible |
| | |
| **Refinement** | |
| Refinement on | $F^2$ |
| $R[F^2>2\sigma(F^2)]$ | 0.063 |
| $wR(F^2)$ | 0.167 |
| $S$ | 1.011 |
| No. of reflections used in refinement | 2147 |
| No. of parameters used | 157 |
| H-atom treatment | H-atom parameters refined independently |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.123P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$ |
| $(\Delta/\sigma)_{max}$ | $-0.111$ |
| $\Delta\rho_{max}$ (e Å$^{-3}$) | 0.85 |
| $\Delta\rho_{min}$ (e Å$^{-3}$) | $-0.79$ |
| Extinction method | None |
| Source of atomic scattering factors | *International Tables for Crystallography* (1992, Vol. C) |
| | |
| **Computer programs** | |
| Structure solution | *SIR*92 (Altomare *et al.*, 1994) |
| Structure refinement | *SHELXL*93 (Sheldrick, 1993), *XRAY*80 (Stewart *et al.*, 1990) |
| Preparation of material for publication | *SHELXL*93 (Sheldrick, 1993) |

Table 2. *Selected geometric parameters (Å², °)*

| | | | |
|---|---|---|---|
| Co1—Cl1 | 2.283 (2) | N2—C5 | 1.492 (9) |
| Co1—Cl2 | 2.293 (2) | C1—C2 | 1.492 (11) |
| Co1—Cl3 | 2.271 (2) | C2—C3 | 1.514 (11) |
| Co1—Cl4 | 2.264 (2) | C3—C4 | 1.510 (10) |
| N1—C1 | 1.495 (10) | C4—C5 | 1.489 (10) |
| | | | |
| Cl4—Co1—Cl3 | 107.97 (8) | C2—C1—N1 | 112.2 (7) |
| Cl4—Co1—Cl1 | 112.44 (7) | C1—C2—C3 | 115.0 (7) |
| Cl3—Co1—Cl1 | 113.55 (8) | C4—C3—C2 | 112.7 (6) |
| Cl4—Co1—Cl2 | 105.79 (7) | C5—C4—C3 | 112.3 (6) |
| Cl3—Co1—Cl2 | 109.84 (8) | C4—C5—N2 | 111.9 (6) |
| Cl1—Co1—Cl2 | 106.96 (8) | | |

Table 3. *Hydrogen-bonding geometry (Å, °)*

| $D—H \cdots A$ | $D—H$ | $H \cdots A$ | $D \cdots A$ | $D—H \cdots A$ |
|---|---|---|---|---|
| N1—H111$\cdots$Cl2[i] | 0.92 (7) | 2.42 (6) | 3.29 (1) | 155 |
| N1—H112$\cdots$Cl1[ii] | 1.00 (10) | 2.3 (1) | 3.29 (1) | 157 |
| N1—H113$\cdots$Cl2[iii] | 0.79 (13) | 2.5 (1) | 3.21 (1) | 155 |
| N2—H223$\cdots$Cl3[iv] | 1.01 | 2.31 | 3.25 (1) | 152 |

Symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x, y, 1 + z$; (iii) $1 + x, y, z$.

Table 4. *Magnetic moments ($\mu$) and Weiss temperatures obtained for the tetrahedral cobalt(II) complexes*

| Compound | $\mu/\mu_B$ | $\theta$ (K) | Temperature range (K) |
|---|---|---|---|
| $C_5H_{16}Cl_4CoN_2$ | 4.57 | −3.62 | 300–3 |
| $C_8H_{22}Cl_4CoN_2$ | 4.63 | −2.70 | 300–5 |
| $C_{10}H_{26}Cl_4CoN_2$ | 4.43 | −4.06 | 300–10 |

Table 5. *DSC data for the three compounds*

Melting point in closed capillary. Endothermic peaks: heating rate 10 K min⁻¹ under a nitrogen atmosphere.

| Compound | Melting point (K) | Heating scan | $\Delta H$ (kJ mol⁻¹) [$T$ (K)] |
|---|---|---|---|
| $C_5H_{16}Cl_4CoN_2$ | 495 ± 2 | 1st | 73.1 [497] |
| | | 2nd | 77.5 [496] |
| $C_8H_{22}Cl_4CoN_2$ | 483 ± 2 | 1st | 9.8 [418]; 1.0 [436]; 1.6 [462]; 19.3 [486] |
| | | 2nd | 9.9 [403]; 12.5 [478]; 11.2 [486] |
| | | 3rd | 15.9 [486] |
| | | 4th | 18.3 [486] |
| $C_{10}H_{26}Cl_4CoN_2$ | 482 ± 2 | 1st | 6.5 [364]; 15.4 [413]; 7.1 [447]; 3.8 [483] |
| | | 2nd | 6.1 [357]; 9.0 [442], 5.0 [482] |
| | | 3rd | 6.1 [357]; 8.6 [441]; 4.8 [482] |

diammonium tetrachlorocobaltate (Smith & Stratton, 1977) or morpholinium tetrachlorocuprates (Marcotrigiano *et al.*, 1976). The compounds corresponding to eight and ten C atoms show a slight splitting for the Co—Cl stretching band. In the cadaverine compound, only a band at 280 cm⁻¹ appears, corresponding to a tetrahedral $CoCl_4^{2-}$ anion. The solid-state visible spectra are consistent with this geometry (Bañares *et al.*, 1984). The MS-FAB+ spectra of the compounds show peaks corresponding to the $[M—HCl]^+$ ions. The observed isotope pattern for this ion closely matches the calculated spectrum (Fig. 3).

Figs. 4 and 5 show the temperature dependence of the magnetic susceptibility of the tetrahedrally coordinated cobalt(II) compounds. In all cases the susceptibility obeys the Curie–Weiss law over a wide temperature range. The calculated magnetic moments are given in
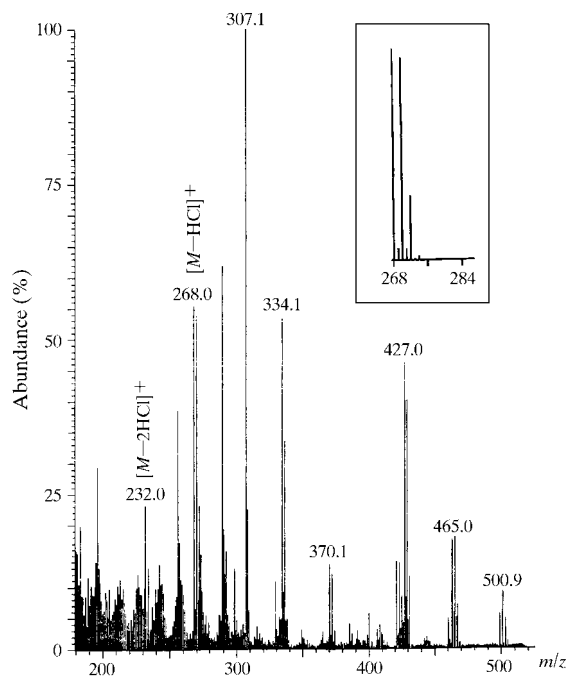


Fig. 3. FAB+/MS spectrum of $[NH_3(CH_2)_5NH_3]CoCl_4$. Inset: calculated isotopic mass distribution for the $[M—HCl]^+$ ion.

Table 4, which shows the values ranging from 4.43$\mu_B$ for the compound with ten C atoms to 4.63$\mu_B$ for the compound with eight C atoms, in agreement with the value obtained for other tetrahedral cobalt(II) compounds. The slightly positive deviations from Curie–Weiss behaviour below 5 K (Fig. 5 inset) and the negative values of the Weiss constants (Table 4) are mainly due to two different factors. First, the deviation can be attributed to the depopulation of the higher level, associated with the $^4A_2$ ground state and giving rise to a decrease in both susceptibility and magnetic moment values, as can be clearly observed in the inset of Fig. 4 showing the $\chi T$ versus $T$ plot. Second, the operativity of antiferromagnetic interactions can be discarded down to 2 K, which is the lower temperature of measurements, since there is no maximum in the $\chi$ versus $T$ plots, and the deviations from linearity of the Curie–Weiss law and the negative values of the Weiss constant are due to the zero-field splitting effect associated with the $^4A_2$ ground state of tetrahedral cobalt(II) compounds.

The maximum *d*-spacings in the X-ray powder diffractograms for compounds with eight and ten C atoms are 10.5 and 12.6 Å, respectively. These spacings may be related to the structure of such systems, which consist of layers of $CoCl_4^{2-}$ sandwiched between hydrocarbon layers formed by the long paraffin chains of $\alpha,\omega$-alkanediammonium groups. Similar spacings are found in analogous tetrachlorozincates of diamines with eight and ten C chains (Busico & Vacatello, 1981). The expected two-dimensional antiferromagnetic interactions for these layered materials should be very weak, since the $CoCl_4^{2-}$ tetrahedra are well separated (Fig. 2). The pathway through the superexchange interactions between the nearest neighbour should be of the type Co—Cl···Cl—Co, with bond angles very different from 180° implying poor overlap between the orbitals involved in the exchange and consequently a very small exchange integral. This reasoning justifies the proposed

absence of interactions down to 2 K. Moreover, our preliminary results (Saez-Puche & Porcher, 1999) in the simulation of the susceptibility of these compounds using the so-called simple overlap model (SOM; Malta, 1982) have successfully reproduced the paramagnetic susceptibility across the whole temperature range of measurements, without invoking the presence of any magnetic interactions.

The thermograms (tg) of the compounds obtained are similar and show no appreciable loss of weight up to 623–673 K. Above this temperature a weight loss occurs, corresponding to sublimation of diamine hydrochloride, identified in the corresponding IR spectrum. All the thermograms show a short plateau concordant with the calculated weight for $CoCl_2$. Finally, at higher temperatures in air all thermograms indicate the formation of $Co_3O_4$, identified by X-ray powder diffraction.
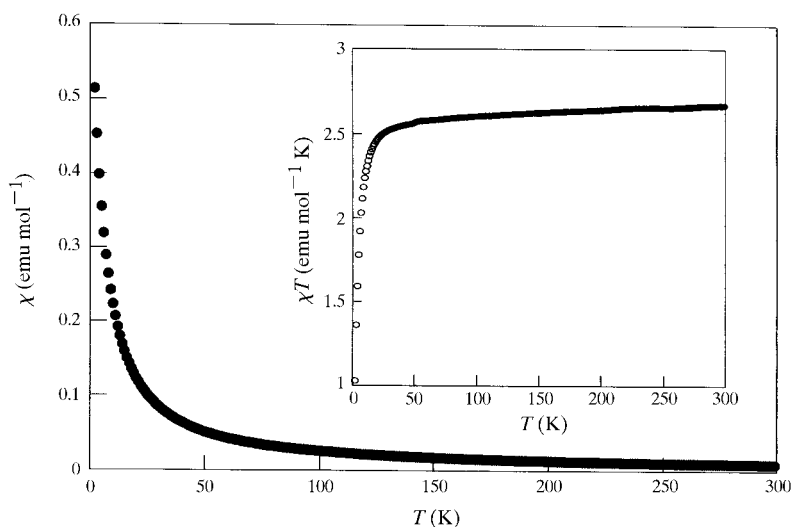


Fig. 4. Variation in molar susceptibility ($\chi$) with temperature for a sample of $[NH_3(CH_2)_8NH_3]CoCl_4$. The inset shows the plot of $\chi T$ versus *T*.
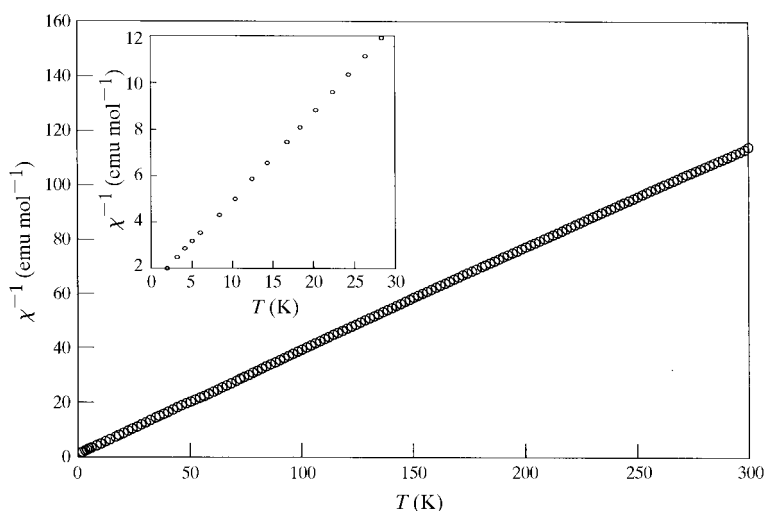


Fig. 5. Temperature dependence of the reciprocal susceptibility ($\chi^{-1}$) for $[NH_3(CH_2)_5NH_3]CoCl_4$. The inset shows an enlargement of the 0–30 K region.

In differential scanning calorimetry (DSC) the existence of an endotherm at ~473 K was noted; this coincides with the melting point measured in a closed capillary tube (Table 5).

The thermal behaviour of freshly prepared compounds is slightly different from that of thermally treated ones (Table 5). In particular, the compounds with eight or ten C atoms show different endothermic processes in successive DSC recordings. Only these compounds show phase transitions in the solid state and greater complexity is observed in the DSC curves, with the appearance of a series of endotherms before the melting point is reached. These peaks are attributed to conformational changes in the polymethylene chains to give forms that are less favoured in terms of energy, but which are generated by a small input of energy. Such transitions have been reported in other alkane diammonium tetrachlorometallates (Busico *et al.*, 1981).

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