gested by SHELX; absolute structure parameter = – 0.05 (4); max./min. residual electron density 0.524/ – 0.501 e Å^{-3}. Since all attempts to obtain X-ray quality crystals of enantiopure **6** failed, (*rac*)-**6** was analyzed: $C_{28}H_{23}F_{12}N_2O_7PRuS_2$, $M_r = 923.64$; orthorhombic, space group *Pbca*; $a = 19.4161(3)$, $b = 15.9196(2)$, $c = 22.0340(3)$ Å, $V = 6810.6(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.802$ g cm^{-3}, $F(000) = 3680$, $\mu = 0.744$ mm^{-1}, crystal size 0.09 × 0.20 × 0.32 mm; of 34713 reflections measured ($-19 \leq h \leq 24$, $-19 \leq k \leq 19$, $-27 \leq l \leq 25$), 6697 were unique; refinement of 485 variables with anisotropic thermal parameters for all non-hydrogen atoms gave $R = 0.0567$, $R_w = 0.1317$, and $S = 1.109$; max./min. residual electron density 0.731/ – 0.709 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102025 ((*S*)-**5**) and CCDC-102024 ((*rac*)-**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[Co$_2^{II}$L(NCS)$_2$(SCN)$_2$]: The First Cobalt Complex to Exhibit Both Exchange Coupling and Spin Crossover Effects[**]

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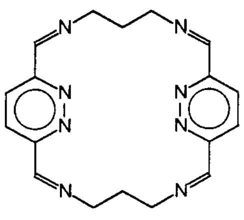
The preparation of molecular materials with possible nanotechnological applications is an area of intense interest.[1, 2] To produce molecules which can act as switches, detectors, or memory devices, the property of bistability is required. Classic examples of bistability are provided by spin-crossover compounds in which the transition from low to high spin is accompanied by a measurable change in magnetism and often also in color.[1–5] Such a signal is vital as it indicates that a change has occurred. To be of use as components there are numerous requirements to be met. One requirement is that the spin crossover should be sharp and occur close to room temperature, ideally with reproducible hysteresis loops (memory) arising from a polymeric structure.[1] Most of the work done in this area has involved iron(II) compounds (d^6), but other transition metals are also known to undergo spin transitions under appropriate conditions, and of interest to us here are cobalt(II) compounds (d^7).

We are studying complexes of chelating ligands based on 3,6-diformylpyridazine.[6–9] To date, very few pyridazine- or phthalazine-bridged dicobalt(II) complexes have been studied,[10] and all of these have contained high-spin cobalt(II) ions throughout the temperature ranges studied. The structure and electrochemistry of the first macrocyclic pyridazine-bridged dicobalt complex was reported very recently.[8] We report here on an air-stable dicobalt(II) complex of the Schiff-base macrocyclic ligand L, which exhibits unique magnetic properties for a cobalt complex and represents a first step towards the development of a "usable" spin-transition polymer.[1]



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The dicobalt(II) complex [Co$_2$L(NCS)$_2$(SCN)$_2$] (**1**) is readily crystallized in quantitative yield by diffusion of a solution of [Co$_2$L(MeCN)$_4$](ClO$_4$)$_4$ (**2**)[8] in acetonitrile into a solution of sodium thiocyanate. The infrared spectrum of **1** shows that the macrocycle has remained intact during this reaction. The structure determination was carried out at 160 K on a crystal obtained from the reaction mixture (Figure 1). The asymmetric unit consists of half of a macrocyclic complex with the other half of the molecule generated by inversion. The

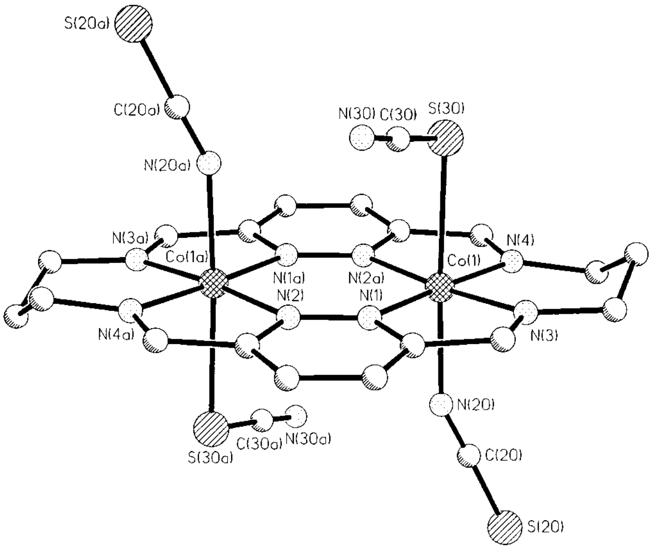

Figure 1. Perspective view of **1**. Selected interatomic distances [Å] and angles [°]: Co(1)–N(4) 1.922(3), Co(1)–N(3) 1.933(3), Co(1)–N(1) 1.966(3), Co(1)–N(2a) 1.983(3), Co(1)–N(20) 2.115(3), Co(1)–S(30) 2.5843(10), Co(1)···Co(1a) 3.813(1); N(4)-Co(1)-N(3) 93.80(12), N(4)-Co(1)-N(1) 175.87(11), N(3)-Co(1)-N(1) 82.07(11), N(4)-Co(1)-N(2a) 81.94(11), N(3)-Co(1)-N(2a) 174.70(11), N(1)-Co(1)-N(2a) 102.19(11), N(4)-Co(1)-N(20) 88.59(12), N(3)-Co(1)-N(20) 90.28(12), N(1)-Co(1)-N(20) 91.21(11), N(2a)-Co(1)-N(20) 92.76(11), N(4)-Co(1)-S(30) 87.49(9), N(3)-Co(1)-S(30) 89.87(9), N(1)-Co(1)-S(30) 92.69(8), N(2a)-Co(1)-S(30) 86.80(8), N(20)-Co(1)-S(30) 176.08(9), N(2)-N(1)-Co(1) 128.5(2), N(1)-N(2)-Co(1a) 129.3(2).

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[**] This work was supported by grants from the University of Otago, the Australian Research Council, and the Bilateral Research Activities Programme (International Science and Technology Linkages Fund). We thank Professor W. T. Robinson (University of Canterbury) for the X-ray data collection.

cobalt(II) ions have distorted octahedral geometries: in each case the basal plane consists of two bridging pyridazine nitrogen donors and two imine nitrogen donors. The axial sites are occupied by two thiocyanate anions, one bound through the N atom and the other through the S atom. The latter feature, S-bound thiocyanate, has not, to our knowledge, been observed before for cobalt(II) compounds.[11] Interestingly, the Co–N_{macro} bond lengths are very similar (av Co–N_{macro} 1.951(4) Å) to those observed at 170 K for the perchlorate analogue **2** (av Co–N_{macro} 1.972(4) Å).[8] In **1** the bond lengths to the thiocyanate axial donors are somewhat longer than the bond lengths to the macrocycle donors, as expected for Jahn-Teller distorted low-spin octahedral d^7 systems (Co–N_{NCS} 2.115(3) Å, difference of 0.164(7) Å): a similar difference is observed in the case of **2** (av Co–N_{MeCN} 2.143(4) Å, difference of 0.171(8) Å). These bond lengths contrast with those recently observed in the high-spin compressed octahedral monocobalt(II) complex [Co(pyridazine)$_4$(NCS)$_2$] (Co–N_{pyrid} 2.199(2), 2.208(2); Co–N_{NCS} 2.057(2) Å).[12] Like **2**, the macrocycle in **1** is very flat with only the central alkyl carbon atoms of the lateral groups displaced substantially from the macrocyclic plane. The pyridazine ring plane and the basal plane of the cobalt atoms are almost coplanar: they intersect at an angle of 3.3°.

The magnetic susceptibility of a sample of [$Co_2L(NCS)_2(SCN)_2$] was determined over the temperature range 4.5–350 K in a field of 1 T. The plots of χ_m and μ_{eff}, per Co atom, as a function of temperature are shown in Figure 2. The susceptibility data are identical in fields of 0.10 and 0.05 T, which indicates that saturation effects are absent. The molecular susceptibility drops slightly as the temperature is lowered from 350 K to 240 K and then increases to a maximum at 10 K before dropping rapidly at temperatures below this. The overall shape of this curve shows that the coupling is antiferromagnetic, and the χ_{max} value, which occurs at 10 K, indicates that the antiferromagnetic coupling is weak. The magnetic moment drops from 3.15 μ_B per Co atom at 350 K to 0.70 μ_B per Co atom at 4.5 K (Figure 2). There is a gently sloping "plateau" from approximately 40 K (1.74 μ_B) to 221 K (1.98 μ_B). But in the high-temperature region, beyond 221 K, the magnetic moment begins to increase noticably, revealing that a gradual spin transition from S = ½ to S = 3/2 takes place. This transition occurs at an encouragingly high temperature; however, the transition is not sharp, but rather occurs over a wide temperature range typical of many, but not all, cobalt(II) d^7 mononuclear crossover systems.[4, 13, 14] The shape of the curve in the plot of magnetic moment versus temperature in the crossover region is affected very little, if at all, by orbital contributions from the high-spin form as judged by comparison with a high-spin analogue of **1** (see above). No hysteresis was observed in the spin-transition region. This is indicative of a lack of intermolecular interactions between dimers.[1] The S = 3/2 states of each Co^{II} ion are not fully populated at 350 K. There is no evidence for two separate crossover transitions per dicobalt(II) complex.

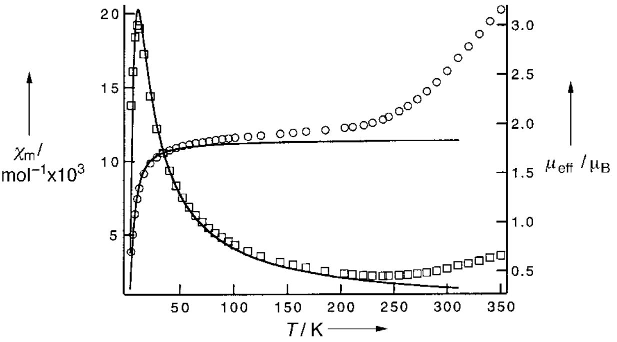

Figure 2. Experimental temperature dependence of χ_m (□) and μ_{eff} (○) per Co atom for **1**. Estimated experimental errors in μ_{eff} are ±0.02 μ_B and in temperature ±0.05 K. The solid lines are the calculated fits of the data to a S = ½ dimer model: $2J = -11.7$ cm^{-1}, $g = 2.13$.

To estimate the degree of exchange coupling at low temperatures, it was assumed that the sample consists of coupled low-spin Co^{II} ions. When only the data from the 4.5 K to 200 K measurements is used, the fit obtained is as shown in Figure 2. The values obtained from the fit are $g = 2.13$ and $2J = -11.7$ cm^{-1}. The g value has been confirmed by measurement of an EPR spectrum of a solid sample of **1** at 77 K, which showed a single broad line of $g = 2.14$. The fit of the low-temperature data is acceptable, with the deviations from calculated values above about 50 K indicative of the presence of the S = 3/2 state and of 3/2–3/2 coupling. There are few low-spin Co^{II} dinuclear species known[14, 15] for comparison to **1**, and these generally have different coordination numbers and hence geometries. For example, in the low-spin five-coordinate complex [Cosalen]$_2$ (salen^{2-} = *N,N'*-ethylenebis(salicylideneiminato) anion) $2J$ is equal to -42 cm^{-1}.[15]

At 350 K the magnetic moment is 3.15 μ_B per Co ion and continues to increase (Figure 2). Based on related monomeric S = 3/2 complexes, the moment could be expected to eventually "plateau" at about 4.2 μ_B.[4, 5] However, the two cobalt ions are antiferromagnetically coupled by the double diazine bridge so the value is likely to be reduced somewhat by this interaction. Interestingly, comparison with related binuclear pyridazine/phthalazine-bridged complexes (all of which are high spin throughout the temperature range studied)[10] also indicates that a value in the range 4.2–4.8 μ_B might be expected.

There is a very real possibility that complexes related to **1**, suitably modified in design, may provide long-range magnetically coupled materials which exhibit spin crossover, and we are actively pursuing this line of research.[9]

Experimental Section

1: A red solution of **2**[8] (0.063 g, 0.073 mmol) in dry acetonitrile (30 mL) was placed in one side arm of an H-tube. Solid sodium thiocyanate (1.00 g, 12.3 mmol) was placed in the other side, and dry acetonitrile was gently layered over both sides until the H-tube was full (ca. 75 mL). After three days the colorless solution contained black crystals of **1** (0.050 g, 98 %). Elemental analysis calcd for $C_{22}H_{20}N_{12}S_4Co_2$: C 37.8, H 2.9, N 24.1, S 18.4; found: C 37.6, H 2.8, N 23.8, S 18.1; IR (KBr): $\tilde{\nu} = 2074, 1624$ cm^{-1}.

Crystal data for **1** ($C_{22}H_{20}N_{12}S_4Co_2$): black square plate, 0.30 × 0.30 × 0.25 mm, monoclinic, space group $P2_1/c$, $a = 9.0179(5)$, $b = 10.7406(5)$, $c = 13.7628(7)$ Å, $\beta = 91.872(1)°$, $V = 1332.3(1)$ Å^3, $Z = 2$, $\mu = 1.60$ mm^{-1}. Data were collected at 160 K on a Bruker SMART diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation. A total of 7790 reflections were collected in the range $4 < 2\theta < 53°$, and the 2568 independent reflections were used in the structural analysis after a semiempirical absorption correction had been applied. The structure was solved by direct methods (SHELXS-97)[16] and refined against all F^2 data (SHELXL-97)[17] to $R1 = 0.047$ (for 2321 $F > 4\sigma(F)$; $wR2 = 0.131$ and GOF = 1.035 for all 2568 F^2;

191 parameters; all non-hydrogen atoms anisotropic). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-102124. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Magnetic susceptibility studies were carried out with a Quantum Design MPMS SQUID magnetometer at an applied field of 1 T. The powdered sample was contained in a calibrated gelatine capsule which was held in the centre of a soda straw fixed to the end of the sample rod. The magnetization values of the instrument were calibrated against a standard palladium sample, supplied by Quantum Design, and also against chemical calibrants such as $CuSO_4 \cdot 5H_2O$ and $[Ni(en)_3](S_2O_3)$ (en = ethylenediamine).

Received: July 7, 1998 [Z12107IE]
German version: *Angew. Chem.* **1999**, *111*, 424–426

Keywords: cobalt · macrocyclic ligands · magnetic properties · Schiff bases · spin crossover

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