The Dithiooxalate-bridged Complex $[Cr(C_2O_2S_2)_3(NiL)_3][ClO_4]_3$ (L = racemic 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane): Synthesis, Crystal Structure and Magnetism†

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The reaction of $KCa[Cr(C_2O_2S_2)_3]\cdot 6H_2O$ ($C_2O_2S_2$ = dithiooxalate) and $[NiL][ClO_4]_2$ (L = racemic 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) in the 1:3 molar ratio gave a chromium(III)trinickel(II) complex $[Cr(C_2O_2S_2)_3(NiL)_3][ClO_4]_3$. It crystallizes with two dimethylformamide and two Pr^{i}OH molecules in the monoclinic space group *C*2/*c*, with *a* = 31.51(1), *b* = 17.447(6), *c* = 19.05(1) Å, β = 112.75(4)° and *Z* = 4. The complex has a $CrNi_3$ core bridged by dithiooxalate groups which bond through sulfur atoms to the Cr and through oxygen atoms to the Ni. The Cr • • • Ni separation is 5.959(5)–5.999(6) Å. The CrS_6 entity shows a distortion to a trigonal-prismatic geometry. Each nickel ion assumes a pseudo-octahedral geometry with two oxygen atoms of the $C_2O_2S_2$ group and four nitrogen atoms of L in a folded form. Cryomagnetic studies (4.2–300 K) revealed a ferromagnetic spin-exchange interaction between the Cr^{III} and Ni^{II} ($J = +5.9$ cm^{-1} based on $\mathcal{H} = -2\Sigma J_{ij}\hat{S}_i\hat{S}_j$).

The study of magnetic spin exchange in polynuclear metal complexes with respect to the electronic structures of the interacting metal ions and the nature of the bridging group is of great value in obtaining a fundamental basis for the development of complex-based ferromagnetic materials.[1-4] The oxalate ($C_2O_4^{2-}$) group can function as a bridge between metal ions leading to polynuclear complexes of oligomeric,[5-10] linear-chain[11] and three-dimensional[4] structures. For the syntheses of three-dimensional mixed-metal assemblies, tris(oxalato)-metalate(III) complexes, $[M(C_2O_4)_3]^{3-}$, have been used as η^3 bridging ligands. Dithiooxalate ($C_2O_2S_2$) bridges in polynuclear metal complexes have received less attention, but the η^2 bridging mode of $[M(C_2O_2S_2)_2]^{2-}$ to form oligonuclear and one-dimensional chain complexes is known.[12-14] The η^3 bridging mode of $[M(C_2O_2S_2)_3]^{3-}$ (M = Cr, Fe, Co, Rh or Al) in a tetranuclear $\{M(C_2O_2S_2)_3M'_3\}$ core was demonstrated for soft Cu^I and Ag^I as M′.[15] For these bridged polynuclear complexes linkage isomerization of the $C_2O_2S_2$ group often occurs. For example, tris(dithiooxalato)ferrate(III) $[Fe(C_2O_2S_2)_3]^{3-}$ has the S,S′ chelation mode[15] but in the tetranuclear complex $[Fe(C_2O_2S_2)_3Ag_3]$ the chelation mode for Fe is O,O′ (and thence S,S′ for Ag).[16] A similar linkage isomerization on going from $[Cr(C_2O_2S_2)_3]^{3-}$ to $[Cr(C_2O_2S_2)_3M_3]$ (M = Cu or Ag) has been reported.[15]

The preparation and magnetic properties of the oxalate-bridged complex $[Cr(C_2O_4)_3(NiL)_3][ClO_4]_3$ (L = racemic 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) were recently reported by Pei *et al.*[9] This complex shows a ferromagnetic spin exchange between the chromium(III) and nickel(II) ions through the oxalate bridge. In this study the corresponding dithiooxalate-bridged complex $[Cr(C_2O_2S_2)_3(NiL)_3][ClO_4]_3$ was prepared and its structure determined by single-crystal X-ray crystallography. The cryomagnetic property of this complex was studied in the temperature range 4.2–300 K in comparison with that of the oxalate complex.

Experimental

Measurements.—Elemental analyses of C, H and N were obtained from the Service Center of Elemental Analysis of Kyushu University. Analyses of metals were made on a Shimadzu AA-680 atomic absorption/flame emission spectrophotometer. Infrared spectra were measured on KBr disks with a JASCO IR-810 spectrometer, electronic spectra on a Shimadzu MPS-2000 multipurpose spectrophotometer. Magnetic susceptibilities were measured on a HOXAN HSM-D SQUID susceptometer in the temperature range 4.2–100 K and on a Faraday balance designed in our laboratory in the range 80–300 K. Calibrations were made with $[Ni(en)_3][S_2O_3]$ (en = ethane-1,2-diamine).[17] Pascal's constants[18] were used for the correction of diamagnetism of constituent atoms.

Materials.—The complexes $KCa[Cr(C_2O_2S_2)_3]\cdot 6H_2O$[19] and $[NiL][ClO_4]_2$[20] were prepared by the literature methods. Tetra-*n*-butylammonium bromide, $MnCl_2\cdot 4H_2O$, and $Cu(NO_3)_2\cdot 3H_2O$ were of reagent grade and used as purchased.

Synthesis.—$[Cr(C_2O_2S_2)_3(NiL)_3][ClO_4]_3$. The complex $[NiL][ClO_4]_2$ (488 mg, 0.9 mmol) was dissolved in a methanol–water mixture (6:4 v/v, 20 cm^3). To this solution was added dropwise a solution of $KCa[Cr(C_2O_2S_2)_3]\cdot 6H_2O$ (180 mg, 0.3 mmol) in methanol–water (6:4 v/v, 15 cm^3), resulting in the immediate precipitation of reddish brown microcrystals. They were separated by suction filtration, washed successively with water and methanol, and dried in a vacuum desiccator. The yield was 292 mg (56%) (Found: C, 37.40; H, 6.15; Cr, 3.10; N,

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† *Supplementary data available* (No. SUP 56964, 4 pp.): magnetic susceptibilities. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

9.55; Ni, 9.80. Calc. for $C_{54}H_{108}Cl_3CrN_{12}Ni_3O_{18}S_6$: C, 37.25; H, 6.25; Cr, 3.00; N, 9.65; Ni, 10.10%). Visible spectrum (powder): 497 and 565 nm. IR (KBr disc): 3245, 2960, 2930, 2875, 1520, 1100 and 620 cm^{-1}.

X-Ray Structural Analysis of $[Cr(C_2O_2S_2)_3(NiL)_3][ClO_4]_3\cdot 2dmf\cdot 2Pr^iOH$.—*Crystal data.* $C_{66}H_{138}Cl_3CrN_{14}Ni_3O_{22}S_6$, $M = 2006.69$, monoclinic, space group $C2/c$, $a = 31.51(1)$, $b = 17.447(6)$, $c = 19.05(1)$ Å, $\beta = 112.75(4)°$, $U = 9661(8)$ Å^3, $Z = 4$, $D_c = 1.38$ g cm^{-3}, $F(000) = 4252$, μ(Mo-Kα) = 9.60 cm^{-1}.

Data collection and reduction. Crystals of the complex were grown as an efflorescent solvate when a dimethylformamide (dmf) solution of it was layered with Pr^{i}OH. Almost all the crystals were unsuitable for X-ray analysis but one with approximate dimensions 0.2 × 0.1 × 0.1 mm was satisfactory. It was sealed in a glass capillary tube and used for intensity and lattice parameter collections with a Rigaku AFC-5 automated four-circle diffractometer, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) at 20 ± 1 °C. For the intensity data collection the ω–2θ scan mode was used at a scan rate of 1° min^{-1}. The intensity data were corrected for Lorentz and polarization factors, but not for absorption. 2420 Independent reflections with $|F_o| > 3\sigma(|F_o|)$ in the range $2.5 \leqslant 2\theta \leqslant 40°$ were assumed to be observed.

The structure was solved by Patterson and Fourier methods. Refinements were carried out by the block-diagonal least-squares method, where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and equal weights ($w = 1$) were adopted for all reflections. Atomic scattering factors were taken from ref. 21. Hydrogen atoms were fixed at the calculated positions and were not refined. The final values of R and R' were 0.0980 and 0.1053, respectively. All the calculations were carried out on a FACOM M-1800/20 computer in the Computer Centre of Kyushu University using a local version[22] of the UNICS III[23] and ORTEP[24] programs. The final positional parameters of the non-hydrogen atoms with their estimated standard deviations are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Structure.—It is presumed that tris(dithiooxalato)chromate(III) $[Cr(C_2O_2S_2)_3]^{3-}$ has the S,S′ chelation mode based on IR spectra.[15] Our X-ray structure analysis for $[Cr(C_2O_2S_2)_3(NiL)_3][ClO_4]_3\cdot 2dmf\cdot 2Pr^iOH$ shows that the Cr^{III} retains the S,S′ chelation mode. An ORTEP view of the complex cation is shown in Fig. 1 together with the numbering scheme. Selected bond lengths and angles are given in Table 2.

The crystal is composed of the tetranuclear complex cation $[Cr(C_2O_2S_2)_3(NiL)_3]^{3+}$, three perchlorate ions, two dmf molecules, and two Pr^{i}OH molecules. The tetranuclear cation is formed by co-ordination of $[Cr(C_2O_2S_2)_3]^{3-}$ to three nickel(II) ions through the outer oxygens of the dithiooxalate groups. The CrS_6 co-ordination sphere has Cr–S bonds ranging from 2.39(1) to 2.40(1) Å. These bonds are significantly long compared with Co–S bonds of $[Co(C_2O_2S_2)_3]^{3-}$ (2.23–2.25 Å)[25] and Ni–S bonds of one-dimensional $NiMn(C_2O_2S_2)_2(H_2O)_{7.5}$ (2.167–2.178 Å).[14] The average S–Cr–S bite angle in the chelates of the $CrNi_3$ complex is 86.5°, smaller than that (89.7°) of $[Co(C_2O_2S_2)_3]^{3-}$,[25] but larger than that (82.4°) of $[Cr(C_2O_4)]_3{}^{3-}$.[26] The CrS_6 co-ordination sphere is distorted towards a trigonal prism. That is, the two triangles defined by S(1), S(2) and S(3′) and S(1′), S(2′) and S(3) are staggered with

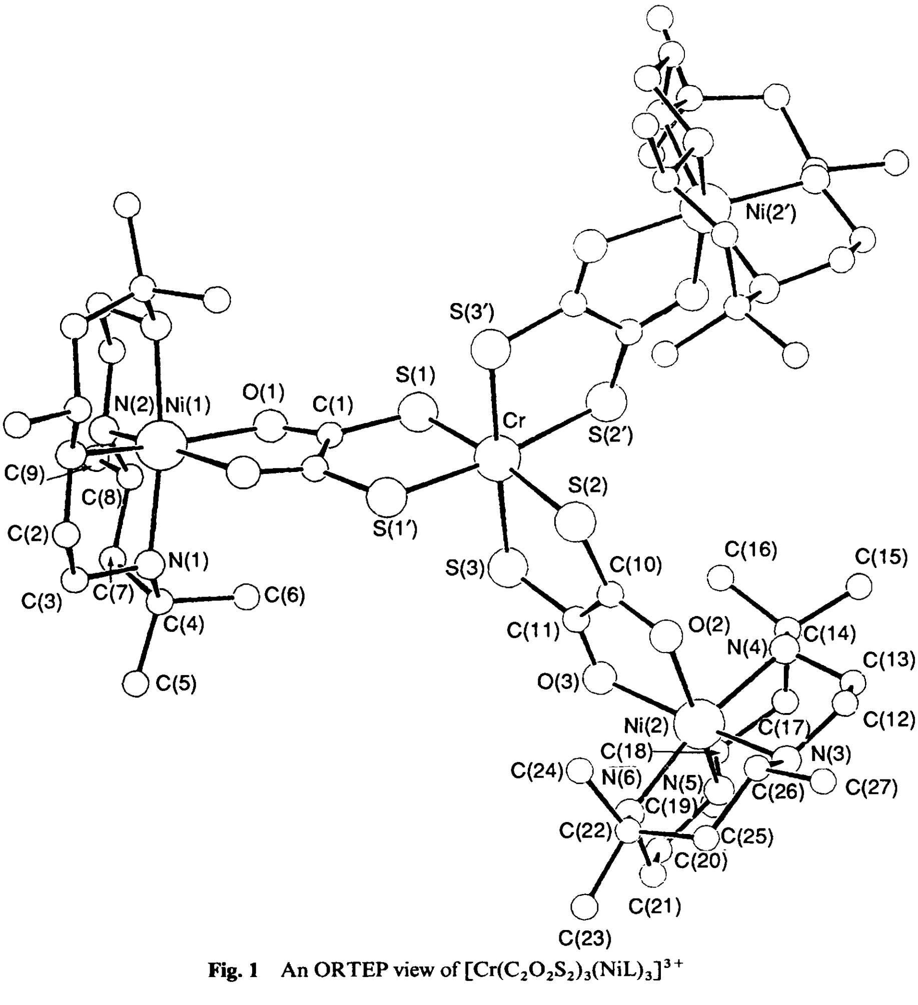

Fig. 1 An ORTEP view of $[Cr(C_2O_2S_2)_3(NiL)_3]^{3+}$

Table 1 Atomic coordinates of non-hydrogen atoms in $[Cr(C_2O_2S_2)_3(NiL)_3][ClO_4]_3\cdot2dmf\cdot2Pr^iOH$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni(1)	0	0.4186(2)	$-\frac{1}{4}$	C(16)	0.1267(9)	−0.126(2)	−0.010(1)
Ni(2)	0.1413(1)	−0.1358(1)	−0.2803(1)	C(17)	0.2020(8)	−0.190(1)	−0.091(1)
Cr	0	0.0745(3)	$-\frac{1}{4}$	C(18)	0.2206(8)	−0.124(1)	−0.124(1)
S(1)	0.0110(2)	0.1741(3)	−0.1581(3)	C(19)	0.2715(8)	−0.112(1)	−0.075(1)
S(2)	0.0001(2)	−0.0215(3)	−0.3404(3)	C(20)	0.2345(8)	−0.086(1)	−0.238(1)
S(3)	0.0823(2)	0.0724(3)	−0.2066(3)	C(21)	0.2148(8)	−0.095(1)	−0.324(1)
O(1)	0.0158(5)	0.3222(8)	−0.1746(8)	C(22)	0.1416(9)	−0.091(1)	−0.443(1)
O(2)	0.0690(5)	−0.1114(7)	−0.3313(8)	C(23)	0.171(1)	−0.053(2)	−0.485(2)
O(3)	0.1341(4)	−0.0257(7)	−0.2358(7)	C(24)	0.097(1)	−0.047(1)	−0.468(1)
N(1)	0.0616(6)	0.428(1)	−0.274(1)	C(25)	0.1355(9)	−0.176(1)	−0.466(1)
N(2)	0.0296(6)	0.4948(9)	−0.158(1)	C(26)	0.1079(8)	−0.222(1)	−0.429(1)
N(3)	0.1353(6)	−0.2373(9)	−0.3451(9)	C(27)	0.095(1)	−0.298(1)	−0.474(2)
N(4)	0.1265(6)	−0.2096(9)	−0.2012(9)	Cl(1)	0	−0.2982(6)	$-\frac{1}{4}$
N(5)	0.2101(6)	−0.1414(9)	−0.2067(9)	O(4)	0	−0.220(2)	$-\frac{1}{4}$
N(6)	0.1653(6)	−0.077(1)	−0.3576(9)	O(5)	0.0413(7)	−0.340(2)	−0.223(2)
C(1)	0.0072(7)	0.256(1)	−0.206(1)	O(6)	−0.001(1)	−0.312(3)	−0.318(3)
C(2)	0.002(1)	0.492(1)	−0.383(1)	Cl(2)	0.2691(3)	−0.3685(6)	−0.1604(5)
C(3)	0.0512(9)	0.495(1)	−0.327(1)	O(7)	0.267(1)	−0.294(1)	−0.185(3)
C(4)	0.1083(8)	0.429(2)	−0.211(2)	O(8)	0.3083(9)	−0.406(1)	−0.164(2)
C(5)	0.1461(9)	0.4493(2)	−0.239(2)	O(9)	0.231(1)	−0.402(2)	−0.225(2)
C(6)	0.1176(9)	0.348(2)	−0.1771(2)	O(10)	0.257(1)	−0.383(3)	−0.104(2)
C(7)	0.1093(9)	0.488(1)	−0.149(2)	O(D)	0.068(1)	0.342(1)	−0.407(2)
C(8)	0.0775(8)	0.478(1)	−0.106(2)	N(D)	0.0605(8)	0.224(1)	−0.451(1)
C(9)	0.097(1)	0.526(1)	−0.032(2)	C(D1)	0.043(1)	0.289(2)	−0.459(3)
C(10)	0.0547(7)	−0.050(1)	−0.309(1)	C(D2)	0.0987(1)	0.212(3)	−0.383(2)
C(11)	0.0934(6)	−0.005(1)	−0.251(1)	C(D3)	0.040(2)	0.162(2)	−0.494(3)
C(12)	0.1131(9)	−0.292(1)	−0.312(1)	O(P)	0.278(1)	0.188(2)	−0.144(2)
C(13)	0.1341(9)	−0.285(1)	−0.228(1)	O(P1)	0.274(2)	0.129(5)	−0.038(4)
C(14)	0.1497(9)	−0.197(1)	−0.114(1)	C(P2)	0.249(2)	0.1539(4)	−0.103(2)
C(15)	0.1388(9)	−0.265(1)	−0.074(1)	C(P3)	0.206(2)	0.1799(4)	−0.142(3)

Table 2 Selected bond distances (Å) and angles (°)

Ni(1)–O(1)	2.14(1)	Ni(2)–N(5)	2.08(2)
Ni(1)–N(1)	2.17(2)	Ni(2)–N(6)	2.15(2)
Ni(1)–N(2)	2.11(2)	Cr–S(1)	2.394(6)
Ni(2)–O(2)	2.14(1)	Cr–S(2)	2.401(7)
Ni(2)–O(3)	2.15(1)	Cr–S(3)	2.394(6)
Ni(2)–N(3)	2.12(2)	Cr ··· Ni(1)	5.999(6)
Ni(2)–N(4)	2.17(2)	Cr ··· Ni(2)	5.959(5)
S(1)–Cr–S(2)	171.8(2)	N(1)–Ni(1)–N(2′)	85.5(8)
S(1)–Cr–S(3)	85.8(2)	N(2)–Ni(1)–N(2′)	102.1(7)
S(1)–Cr–S(1′)	87.0(2)	O(2)–Ni(2)–N(3)	93.5(6)
S(1)–Cr–S(2′)	91.2(2)	O(2)–Ni(2)–N(4)	87.5(6)
S(1)–Cr–S(3′)	95.5(2)	O(2)–Ni(2)–N(5)	164.2(7)
S(2)–Cr–S(3)	86.3(2)	O(2)–Ni(2)–N(6)	100.9(6)
S(2)–Cr–S(2′)	91.7(3)	O(3)–Ni(2)–N(3)	167.4(5)
S(2)–Cr–S(3′)	92.5(2)	O(3)–Ni(2)–N(4)	100.0(6)
S(3)–Cr–S(3′)	178.3(3)	O(3)–Ni(2)–N(5)	91.0(5)
O(1)–Ni(1)–O(1′)	76.6(5)	O(3)–Ni(2)–N(6)	88.0(7)
O(1)–Ni(1)–N(1)	101.8(7)	N(3)–Ni(2)–N(4)	85.1(7)
O(1)–Ni(1)–N(2)	91.2(6)	N(3)–Ni(2)–N(5)	100.8(7)
O(1)–Ni(1)–N(1′)	84.7(7)	N(3)–Ni(2)–N(6)	88.4(7)
O(1)–Ni(1)–N(2′)	164.9(6)	N(4)–Ni(2)–N(5)	87.2(6)
N(1)–Ni(1)–N(2)	89.4(8)	N(4)–Ni(2)–N(6)	169.7(7)
N(1)–Ni(1)–N(1′)	171.8(7)	N(5)–Ni(2)–N(6)	86.2(7)

respect to the pseudo-C_3 axis of the complex cation (see Fig. 2), with a rotation angle of 53.6°, smaller than the 60° for a regular octahedron. Such a distortion is commonly seen for tris(chelate) complexes.[25–27]

The surroundings about each Ni^{II} are *cis*-β-octahedral with four nitrogens of L in a folded form and two oxygens of the bridging $C_2O_2S_2$ group. The Ni–O bond distances fall in the range 2.14(1)–2.16(1) Å, slightly elongated relative to these in oxalate-bridged dinuclear nickel(II) complexes.[28,29] The Ni–N bond distances range 2.08(2) to 2.17(1) Å. The Cr ··· Ni separation is on average 5.98 Å.

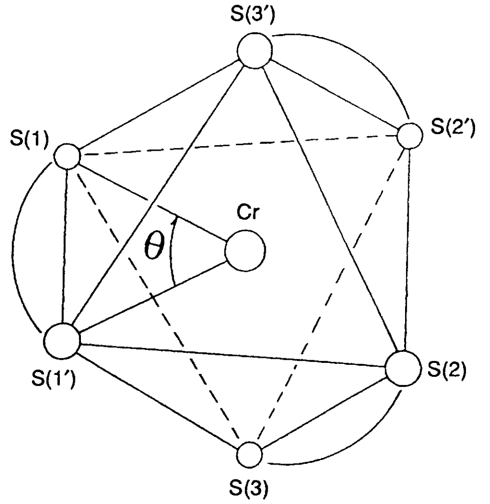

Fig. 2 Schematic representation of distortion of the CrS_6 coordination sphere towards a trigonal prism

Magnetism.—The magnetic properties of this complex were studied in the range 4.2–300 K and the results are given in Fig. 3 in the form of plots of χ_M^{-1} *vs.* T and μ_{eff} *vs.* T where χ_M and μ_{eff} are the magnetic susceptibility and magnetic moment per $CrNi_3$, respectively. The Curie–Weiss plot of the magnetic susceptibility is linear in the range 75–300 K with a positive Weiss constant $\theta = +23$ K [based on $\chi_M^{-1} = (T - \theta)/C$], suggesting a ferromagnetic spin-exchange interaction within the $Cr^{III}Ni^{II}_3$ core. The magnetic moment at room temperature is 6.69 μ_B which is larger than the spin-only value 6.25 μ_B expected from the expression $\mu_{eff}^2 = \mu_{Cr}^2 + 3\mu_{Ni}^2$ with $\mu_{Cr} = 3.87$ μ_B and $\mu_{Ni} = 2.83$ μ_B. When the temperature is lowered the moment increases to the maximum value of 10.2 μ_B at 7.2 K and then tends to decrease below this temperature. The maximum value is very close to the spin-only value 9.95 μ_B for $S = \frac{9}{2}$, indicating that the spins of the chromium(III) and nickel(II) ions are coupled ferromagnetically at *ca.* 7 K. The reduction in

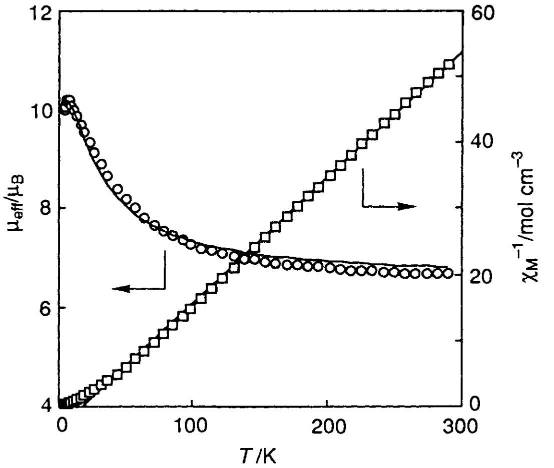

Fig. 3 Temperature variations of the magnetic moment (○) and inverse magnetic susceptibility (□) of the $CrNi_3$ complex

magnetic moment below 5 K may be attributed to a secondary effect such as zero-field splitting or intermolecular magnetic interaction.

In order to analyse the cryomagnetic behaviour of the complex the Heisenberg model ($\mathcal{H} = -2\Sigma J_{ij}\hat{S}_i\hat{S}_j$) was adopted and an intermolecular interaction (zJ') considered as the origin for the reduction in magnetic moment below 5 K. Such a magnetic treatment was successfully applied by Pei *et al.*[9] to $[Cr(C_2O_2S_2)_3(NiL)_3][ClO_4]_3$. Using the magnetic expression derived by Pei *et al.* the magnetic behaviour of the present complex can be reproduced as shown in Fig. 3, using the parameters $J = +5.9$ cm^{-1}, $g_{Cr} = 1.98$, $g_{Ni} = 2.15$ and $zJ' = -0.79$ cm^{-1}. The discrepancy factor defined by the expression $[\Sigma(\mu_{obs} - \mu_{calc})^2/\Sigma\mu_{obs}^2]^{\frac{1}{2}}$ is 1.7×10^{-2}.

The ferromagnetic interaction in this complex can be understood in terms of strict orthogonality of the magnetic orbitals of the metal ions.[30,31] That is, Cr^{III} in a pseudo-octahedral environment has three unpaired electrons in π-type magnetic orbitals associated with t_{2g} metal orbitals, whereas Ni^{II} has two unpaired electrons in σ-type magnetic orbitals associated with e_g metal orbitals, so that the magnetic orbitals of the two metal ions cannot overlap through the dithiooxalate bridge. In the related oxalate complex[9] the magnetic interaction between the Cr^{III} and Ni^{II} through the oxalate bridge is also ferromagnetic but the evaluated exchange integral is smaller ($J = +2.65$ cm^{-1}). The enhanced ferromagnetic interaction in the present complex may be ascribed to the high 'nephelauxetic effect' of the sulfur donor atom,[32] allowing a large interaction between the magnetic orbitals. It has been revealed by this study that the dithiooxalate bridge is a more efficient magnetic mediator than the oxalate bridge in the chromium(III)–nickel(II) system.

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