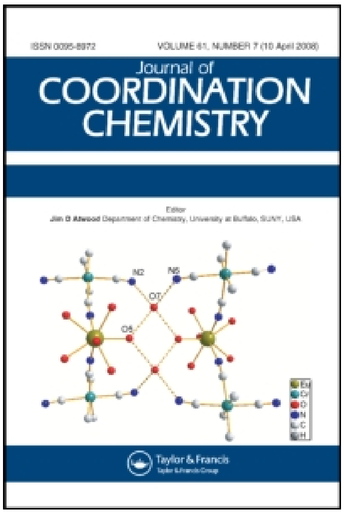

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SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF A NOVEL CYANO-BRIDGED BINUCLEAR CHROMIUM(III) COMPLEX OF A TETRADENTATE SCHIFF BASE

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SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF A NOVEL CYANO-BRIDGED BINUCLEAR CHROMIUM(III) COMPLEX OF A TETRADENTATE SCHIFF BASE

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The complex $[Bu_4N][\{Cr(salen)CN\}_2CN]\cdot 4H_2O$ (H_2salen = *N,N'*-ethylene*bis*(salicylideneiminato)) has been prepared by the reaction of $[Cr(salen)(H_2O)_2]NO_3$ with NaCN. X-ray crystal structure analysis revealed the constituents to be binuclear anions, $[\{Cr(salen)CN\}_2CN]^-$, Bu_4N^+ cations and H_2O molecules. The two Cr(III) atoms are bridged by a CN^- ion in *trans*-mode. The geometry around each Cr(III) atom is approximately octahedral. The equatorial plane at each Cr(III) is composed of the N_2O_2 donor atoms of the tetradentate salen ligand. Axial sites are occupied by a terminal and a bridging CN group. The temperature dependence of the magnetic susceptibility indicates a weak antiferromagnetic interaction through the cyano bridge; an exchange parameter of $-5.7\ cm^{-1}$ is close to those of other μ-CN chromium(III) complexes.

Keywords: chromium(III); cyano-Bridge; tetradentate Schiff base; *N,N'*-ethylene*bis*(salicylideneiminato); binuclear complex; crystal structure

INTRODUCTION

Chromium complexes with cyano-bridges are relatively new. The introduction of the cyano ligand brings about special changes in the properties of Cr(III) complexes such as their charge-transfer nature, hence making CN^- stand out among other common ligands [1]. The magnetic interaction of Cr(III) complexes

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with cyano-bridges has also aroused wide interest [2,3]. To now, a number of cyano-bridged chromium homonuclear and heteronuclear complexes have been synthesized [4-10]. Most of these complexes are heteronuclear in nature. For example, a trinuclear complex $[\{trans\text{-}(NC)(cyclam)Cr(\mu\text{-}CN)\}_2Ru(bpy)_2](PF_6)_4$ has been synthesized and its X-ray structure investigated by Bignozzi *et al.* [8, 9]. However, dinuclear Cr(III) complexes with a single μ-cyano ligand are rare, and only a few examples containing amine ligands have been reported [1-3]. To our knowledge, no crystal structure of a dinuclear chromium complex with a μ-cyano ligand has been reported. In this paper, the first binuclear μ-cyano chromium(III) Schiff base complex $[Bu_4N][\{Cr(salen)CN\}_2CN]\cdot 4H_2O$ (H_2salen = *N,N′*-ethylene*bis*(salicylideneiminato)) is reported and its crystal structure and magnetic properties investigated. The Cr(salen)CN unit is bridged by a CN ligand in *trans*-mode. The molecule has two terminal CN ligands which are potential bridging agents suitable for further formation of heterometallic chain complexes.

EXPERIMENTAL

Chemicals

Reagents and solvents were of chemical grade and were used without further purification. The $[Cr(salen)(H_2O)_2]NO_3$ complex was prepared according to the literature [11]. CAUTION: sodium cyanide is extremely toxic and must be treated with extreme care in all experimental processes.

Preparations of Complex

$[Bu_4N][\{Cr(salen)CN\}_2CN]\cdot 4H_2O$

$[Cr(salen)(H_2O)_2]NO_3$ (1 mmol) was dissolved in 20 cm^3 of methanol. A methanol solution (10 cm^3) of NaCN (4 mmol) including a small quantity of water was added and the mixture was refluxed for 2h. The flask was allowed to cool to ambient temperature and the contents filtered. To the filtrate was added a methanol solution (5 cm^3) of Bu_4NBr (1 mmol). The solution was left to stand for several days and then reddish brown crystals (suitable for X-ray analysis) were collected. *Anal.* Calcd. for $C_{51}H_{72}CrN_8O_8$ (%): C, 59.51; H, 7.05; N, 10.89; Found: C, 59.14; H, 7.31; N, 10.46.

Physical Measurements

All elemental analyses were carried out at the Analysis and Measurement Centre of Nanjing University. Infrared spectra were recorded in the 4000-400 cm^{-1}

region using KBr pellets on a Bruker IFS 66V spectrophotometer. Magnetic susceptibilities of powder samples were measured in the temperature range 4.2-80 K by means of a vibrating sample magnetometer (Model CF1) and by the Faraday method in the temperature range 80-300K. $Ni(en)_3(S_2O_3)$ (en = ethylenediamine) was used as susceptibility standard. Susceptibilities were corrected for diamagnetism of substituent atoms using Pascal's constant.

X-ray Structure Determination

Single crystals of $[Bu_4N][\{Cr(salen)CN\}_2CN]$ suitable for X-ray diffraction study were grown from methanol solution. A flat needle of approximate dimensions 0.1×0.2×0.3 mm was used for data collection and cell parameter determination on a four-circle CAD4 diffractometer with MoKα radiation (λ = 0.71073Å) at room temperature (27°C). Crystallographic and refinement data are presented in Table I. Data were collected using the ω-2θ scan method and were processed for Lorentz polarization effects. Empirical absorption correction was made by means of the psi-scan technique.

The absolute structure was solved by the Patterson method using the SHELXS 86 computer program [12]. All non-hydrogen atoms except for C11, a butyl chain (C1a-C4a) and the four disordered water molecules were subjected to anisotropic

TABLE I Crystallographic and refinement data.

Crystal data	
Formula	$C_{51}H_{72}Cr_2N_8O_8$
Formula weight	1029.17
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 13.719(1)Å Z = 2
	b = 13.849(2)Å β = 95.070(7)°
	c = 14.419(1)Å V = 2728.8(5) Å^3
D_c (g·cm^{-1})	1.253
μ(mm^{-1})	0.455
Data collection	
Θ range for data collection	1.42 to 25.00°
Collection ranges	$-16<=h<=16$, $0<=k<=16$, $-17<=l<=17$
Total reflections collected	5223
Independent reflections [$I \geq 2\sigma(I)$]	5019 (R_{int} = 6.83%)
Structure determination and refinement	
No. of variables:	605
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.892
Final R indices for [$I > 2\sigma(I)$]	R = 0.089, R_w = 0.153

TABLE II Final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the title complex.

	x/a	*y/b*	*z/c*	*U(eq)*
Cr(1)	9121(2)	10007(2)	9105(2)	64(1)
Cr(2)	6071(2)	8704(2)	6945(2)	60(1)
O(1)	9014(7)	11366(8)	8932(6)	61(3)
O(2)	8289(7)	9901(8)	10125(6)	66(3)
N(1)	9942(10)	9863(13)	8036(10)	76(5)
N(2)	9339(11)	8541(10)	9179(10)	67(4)
C(1)	9575(13)	11922(14)	8466(11)	65(5)
C(2)	9501(12)	12922(15)	8585(12)	72(5)
C(3)	10756(14)	12237(23)	7360(15)	114(8)
C(4)	10673(18)	13190(23)	7442(18)	117(9)
C(5)	10032(16)	13536(15)	8091(16)	100(7)
C(6)	10243(11)	11557(16)	7814(13)	72(5)
C(7)	10373(12)	10538(16)	7654(13)	78(6)
C(8)	10104(11)	8908(16)	7779(14)	89(7)
C(9)	10166(14)	8291(14)	8660(16)	106(8)
C(10)	8855(13)	7952(15)	9609(13)	83(6)
C(11)	8076(13)	8135(14)	10137(11)	61(5)
C(12)	7569(16)	7405(15)	10468(13)	103(8)
C(13)	6815(21)	7516(23)	10975(16)	136(12)
C(14)	6561(17)	8446(18)	11222(12)	106(8)
C(15)	7030(13)	9213(18)	10925(10)	96(7)
C(16)	7824(13)	9111(12)	10396(11)	65(5)
O(1′)	6989(8)	8208(7)	6118(7)	62(3)
O(2′)	5695(7)	9816(9)	6243(6)	74(3)
N(1′)	6387(11)	7554(10)	7789(8)	57(4)
N(2′)	5192(9)	9086(10)	7912(7)	61(4)
C(1′)	7735(14)	7683(13)	6342(13)	71(5)
C(2′)	8518(14)	7608(13)	5734(13)	82(5)
C(3′)	9279(16)	6999(17)	5935(17)	109(7)
C(4′)	9300(19)	6459(18)	6746(19)	126(9)
C(5′)	8577(18)	6428(17)	7307(14)	107(7)
C(6′)	7803(13)	7059(14)	7123(16)	77(6)
C(7′)	7142(17)	6980(15)	7794(15)	87(7)
C(8′)	5636(13)	7454(14)	8451(12)	92(6)
C(9′)	5356(12)	8479(16)	8748(10)	97(7)
C(10′)	4505(11)	9699(14)	7827(11)	72(6)
C(11′)	4284(12)	10318(13)	7004(11)	76(6)
C(12′)	3455(13)	10910(17)	6977(16)	108(7)
C(13′)	3248(16)	11546(16)	6279(17)	110(8)
C(14′)	3812(15)	11530(15)	5540(15)	94(6)
C(15′)	4602(10)	10933(14)	5538(12)	76(6)
C(16′)	4925(12)	10309(11)	6272(11)	58(5)
N(3)	11104(11)	10312(13)	10401(10)	110(7)
N(4)	7855(10)	9687(10)	8174(9)	70(4)
N(5)	4150(11)	7591(11)	6083(9)	80(4)
C(17)	10385(12)	10183(15)	9992(11)	83(6)
C(18)	7203(11)	9416(12)	7698(9)	55(5)

TABLE II *(continued)* Final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the title complex.

	x/a	*y/b*	*z/c*	*U(eq)*
C(19)	4861(13)	7993(13)	6335(10)	65(5)
N	6845(10)	12933(12)	6610(9)	81(5)
C(1A)	7488(25)	13888(26)	6299(25)	53(11)
C(1A′)	7698(30)	13582(33)	6520(27)	77(14)
C(1B)	7018(14)	11968(14)	6115(12)	88(6)
C(1C)	6946(14)	12753(16)	7641(13)	100(7)
C(1D)	5806(14)	13242(17)	6310(12)	90(7)
C(2A)	7677(30)	13799(36)	5457(30)	86(14)
C(2A′)	7323(32)	14029(36)	5228(29)	100(17)
C(2B)	8000(13)	11560(18)	6276(15)	111(8)
C(2C)	6281(13)	12031(16)	8039(11)	94(6)
C(2D)	5481(15)	14156(18)	6691(15)	112(7)
C(3A)	8249(24)	14621(25)	5156(22)	202(13)
C(3B)	8075(19)	10641(23)	5690(18)	149(10)
C(3C)	6511(15)	12077(21)	9101(13)	134(10)
C(3D)	4416(18)	14318(15)	6497(14)	118(7)
C(4A)	8867(35)	14488(35)	4518(34)	137(17)
C(4A′)	9175(29)	14148(31)	5150(29)	110(14)
C(4B)	8194(22)	10731(21)	4819(20)	191(12)
C(4C)	5914(17)	11384(20)	9541(14)	156(10)
C(4D)	4032(18)	15222(15)	6894(16)	167(11)
O′A	7214(41)	13014(42)	11412(42)	186(22)
O′B	7349(19)	12920(20)	12378(20)	182(10)
O″A	12852(35)	9601(37)	9586(37)	184(20)
O″B	12561(24)	9482(25)	8958(24)	185(14)
O‴A	8374(20)	11269(22)	11571(21)	128(10)
O‴B	8212(21)	11615(24)	10952(22)	136(11)
O(0A)	13136(25)	9879(28)	10914(22)	266(14)
O(0B)	14236(65)	9968(76)	10834(56)	236(33)

refinement. The site occupancy of the disordered butyl chain was fixed at 0.5 while those of the water molecules range from 25 to 75%. Hydrogen atoms were generated geometrically and were allowed to ride on their respective parent atoms. Hydrogen atoms on the disordered atoms were omitted. Final refinement using full-matrix least-squares converged to $R = 0.089$, $R_w = 0.153$. High angle reflections were weak resulting in high R factors. Final values of refined atomic positional parameters (with e.s.d.s) are listed in Table II. Electron density Fourier-difference syntheses allocated maximum and minimum residual peaks of 0.302 and -0.247 eÅ^{-3}. Crystallographic computations were performed using the SHELXL 93 package on a 486 PC [13]. The numbering scheme is shown in Figure 1. Selected bond distances and angles are presented in Table III.

TABLE III Selected bond distances (Å) and angles (°).

Cr(1)-O(1)	1.903(11)	Cr(1)-O(2)	1.945(10)
Cr(1)-N(1)	1.998(14)	Cr(1)-N(2)	2.053(14)
Cr(1)-C(17)	2.08(2)	Cr(1)-N(4)	2.14(2)
Cr(2)-O(2')	1.889(11)	Cr(2)-O(1')	1.936(10)
Cr(2)-N(2')	1.993(11)	Cr(2)-N(1')	2.027(13)
Cr(2)-C(19)	2.06(2)	Cr(2)-C(18)	2.06(2)
O(1)-C(1)	1.31(2)	O(2)-C(16)	1.34(2)
N(1)-C(7)	1.26(2)	N(1)-C(8)	1.49(2)
N(2)-C(10)	1.25(2)	N(2)-C(9)	1.45(2)
C(8)-C(9)	1.53(2)	C(8')-C(9')	1.54(2)
N(3)-C(17)	1.12(2)	N(4)-C(18)	1.14(2)
N(5)-C(19)	1.15(2)		
O(1)-Cr(1)-O(2)	97.5(5)	O(1)-Cr(1)-N(1)	92.2(6)
O(2)-Cr(1)-N(1)	169.9(7)	O(1)-Cr(1)-N(2)	173.7(6)
O(2)-Cr(1)-N(2)	88.8(6)	N(1)-Cr(1)-N(2)	81.5(7)
O(1)-Cr(1)-C(17)	93.3(5)	N(1)-Cr(1)-C(17)	89.4(6)
N(2)-Cr(1)-C(17)	88.5(7)	O(1)-Cr(1)-N(4)	94.2(4)
O(2)-Cr(1)-N(4)	87.8(4)	N(1)-Cr(1)-N(4)	88.7(5)
N(2)-Cr(1)-N(4)	86.3(5)	C(17)-Cr(1)-N(4)	174.7(7)
O(2')-Cr(2)-O(1')	97.0(4)	O(2')-Cr(2)-N(2')	90.3(5)
O(1')-Cr(2)-N(2')	172.7(6)	O(2')-Cr(2)-N(1')	174.5(5)
N(1')-Cr(2)-C(18)	87.1(6)	C(19)-Cr(2)-C(18)	173.3(6)
C(18)-N(4)-Cr(1)	172.7(14)	N(3)-C(17)-Cr(1)	174(2)
N(4)-C(18)-Cr(2)	170(2)	N(5)-C(19)-Cr(2)	173.0(14)

RESULTS AND DISCUSSION

Description of the Structure

The unit cell contents consist of dinuclear anions, $[\{Cr(salen)CN\}_2CN]^-$, Bu_4N^+ cations and H_2O molecules. The geometry about the two Cr(III) centers is approximately octahedral. The ligating atoms at Cr(1) are similar to those at Cr(2), except for the bridging cyanide ligand which uses its C atom to bond to Cr(2) and N atom to Cr(1). The bond distances of Cr(1)-N(1) (1.998(14)Å), Cr(1)-N(2) (2.05(1)Å), Cr(1)-O(1) (1.90(1)Å) and Cr(1)-O(2) (1.95(1)Å) in the equatorial plane are close to those in $K[Cr(salen)(NCS)_2]$ [14]. The corresponding bond distances at Cr(2) fall in the same range as for Cr(1) (1.89(1)Å-2.03(1)Å). The longest Cr-N bond is Cr(1)-N(4) (2.14(2)Å), N(4) being the N atom of the bridging CN ligand. Two terminal cyano ligands bond to Cr(1) and Cr(2) *via* carbon. The average length (2.07(2)Å) is similar to that of the bridging CN ligand, Cr(2)-C(18) (2.06(2)Å). It is noteworthy that the Cr-CN bond lengths are about 0.07Å shorter than the Cr-NC bond. A similar trend occurs in other CN-bridged complexes, such as $Ru(bpy)_2[Cr(cyclam)(CN)_2]_2^{4+}$ and $(NH_3)_5CoNCCo(CN)_5$ [9,15]. The bond angles N(3)-C(17)-Cr(1), Cr(1)-N(4)-

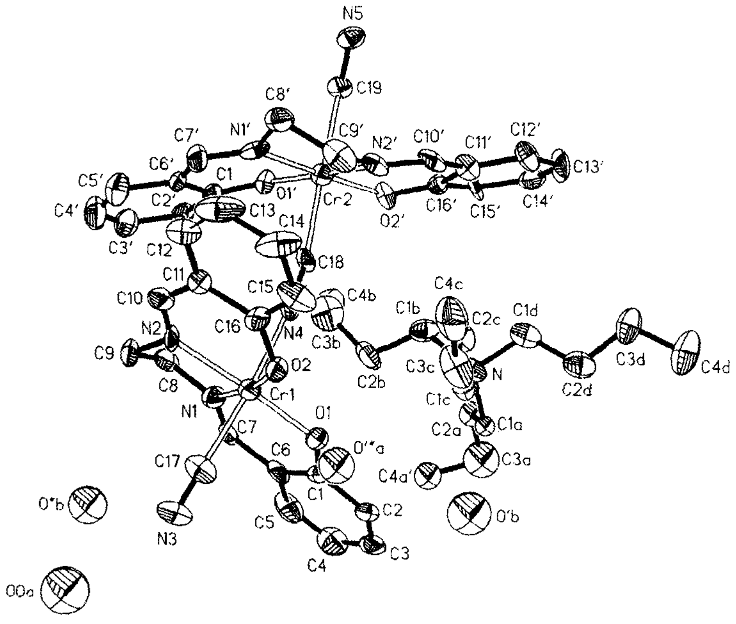

FIGURE 1 A perspective drawing and the numbering scheme of the title complex.

C(18), N(4)-C(18)-Cr(2) and N(5)-C(19)-Cr(2) are 174(2), 173(1), 170(2) and 173(1)°, respectively, showing these atoms are more or less colinear (see Figure 2). Comparing the bond angles ∠CoCN (172.4(3)°) and ∠CoNC (159.8(3)°) in the analogous Co(III) complex $[(NH_3)_5CoNCCo(CN)_5]$, the title Cr(III) complex shows better linearity. This is in agreement with the conclusion drawn by Glerup *et al.* [3]. Another feature noted from Figures 1 and 2 is that the two N_2O_2 planes of the tetradentate Schiff base salen ligand at Cr1 and Cr2 are not parallel, the interplanar angle being 39.3(2)°.

The water molecules in the unit cell form H bonds linking the anions. The H-bonding scheme is shown in Figure 2 and a list of probable hydrogen bonds is given in Table IV.

IR Spectra

The IR bands due to CN stretching are diagnostically useful for distinguishing terminal CN from the bridging CN group [16]. In dinuclear complexes with bridging CN there is a significant difference with respect to the terminal CN ligand. The clear splitting of the CN stretching frequencies is good evidence for a bridging cyano group. According to literature data, the component occuring at lower frequency is assigned to ν(CN) of the terminal cyano group (2130-2135 cm^{-1}), while that appearing at high frequency is attributed to the bridging cyano group (2160-2180 cm^{-1}) [17, 6]. Recently, Bignizzi researched the IR spectra of *cis*-$[Ru(bipy)_2\{$*trans*-$Cr(cyclam)(CN)_2\}_2]^{4+}$ and suggested that the degree of bond weakening induced by back donation from the metal may affect the frequencies and intensities of the IR bands [18]. The IR spectra of the title complex show two bands at 2152 cm^{-1} (medium intensity) and 2138 cm^{-1} (weak intensity). The higher frequency may be assigned to ν(CN) of bridging CN and the lower frequency to the terminal ν(CN).

Magnetic Susceptibility

Measurements of magnetic susceptibility indicate that the effective magnetic moment declines from 3.65 B.M. at room temperature to 0.717 B.M. at 4.2K. Antiferromagnetic exchange interactions between Cr atoms can lower the μ_{eff} value as compared to the calculated "spin-only" value of 3.87 B.M. for a d^3

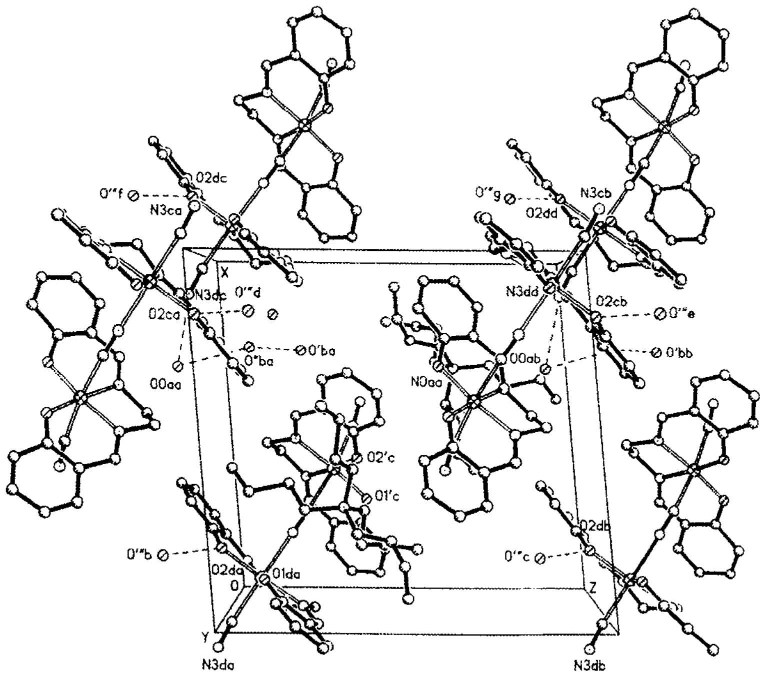

FIGURE 2 Packing diagram viewed down the *b* axis.

TABLE IV Probable A-H...B hydrogen bonds (Å) in the structure.

OA...N3	2.883	O'B†...O"B	2.906
OA...O"B	2.913	O'B...O'''A	2.976
OB...O"A	2.549	O"A...N3	2.933
O'A†;...O"A	2.624	O'''A...O2	2.811
O'A...O'''A	2.892	O'''B...O2	2.662
O'A...O'''B	2.497		

†Symmetry transformation 2 − *x*, −1/2 + *y*, 2 − *z*.

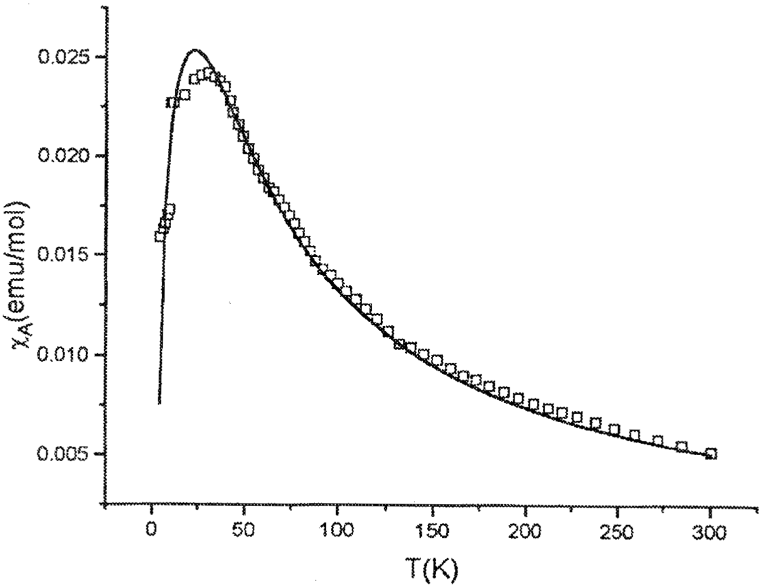

FIGURE 3 Temperature dependence of the magnetic susceptibility of the title complex.

system [19, 20]. The magnetic moment of the title complex is close to that of $M^I[Fe(en\ or\ tn)_2Cr(CN)Cr(CN)_5^-]$ ($\mu_{eff} = 3.40\ \mu_B$ at 300 K and $2.22\mu_B$ at 80 K) [2]. The measurements can be analyzed by using the spin-spin interaction Hamiltonian, $H = -2JS_1 \cdot S_2$. The susceptibility per atom (χ_A) of an $S_1 = S_2 = 3/2$ exchange coupling dimer is given by the following equation [21],

$$\chi_A = \frac{N\beta^2 g^2}{3kT} \cdot \frac{\exp(2J/kT) + 5\exp(6J/kT) + 14\exp(12J/kT)}{1 + 3\exp(2J/kT) + 5\exp(6J/kT) + 7\exp(12J/kT)}$$

where all parameters have their usual meanings. Experimental values are interpreted in terms of the above equation as shown in Figure 3. The solid curve is calculated using the parameters, $J = -5.7\ cm^{-1}$ and $g = 1.96$, indicating that a weak antiferromagnetic superexchange interaction is exerted between the two chromium(III) ions through the μ-CN group. The J value is slightly larger than those of cis-K[F(NN)$_2$Cr(μ-NC)Cr(CN)$_5$] with NN = en or tn (J = -1.4 cm^{-1} and -1.2 cm^{-1}, respectively) [22] and smaller than those of [(NH$_3$)$_5$Cr(μ-CN)Cr(NH$_3$)$_5$](ClO$_4$)$_5$·4H$_2$O (J = -16.2 cm^{-1}) [3] and *cis*-K[Fe(NN)$_2$Cr(μ-NC)CrNO(CN)$_4$] (M = K$^+$, Na$^+$, NH$_4$$^+$, NN = en, tn) (J = -20 cm^{-1}) [2]. More structural information is needed to explain the different J values of CN-bridged dinuclear Cr(III) complexes.

SUPPLEMENTARY DATA

Additional material consisting of H atom coordinates, anisotropic thermal parameters, observed and calculated structure factors, a complete list of bond distances and magnetic susceptibility data are available from the authors on request.

Acknowledgements

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