Synthesis and Magnetic Properties of a Polymeric Nitridochromium(V) Complex with a Tetradentate Schiff Base Ligand

Masanobu Tsuchimoto,*[a] Naoki Yoshioka,*[b] and Shigeru Ohba[a]

Keywords: Nitrides / Chromium / Polymers / Schiff bases / Magnetic properties

A novel polymeric nitridochromium(V) complex with a Schiff base ligand [CrN(salpn)] [H_2(salpn) = *N,N′*-disalicylidene-1,3-propanediamine] was prepared by photolysis of an azidochromium(III) complex in acetonitrile. X-ray crystal structure analyses of the starting material $\{(CH_3)_2NH_2\}_2[CrCl_2(salpn)]Cl$ (**1**) and the polymeric complex [CrN(salpn)] (**3**) were carried out. The orange complex **3** has a linear ···Cr≡N···Cr≡N··· chain structure with the N···Cr distance being 2.508(2) Å. Magnetic data show that **3** has a ferromagnetic intermolecular interaction in the chains (J = +8.4 cm^{-1}).

Introduction

The synthesis of new linear-chain polynuclear metal complexes is important because of their physical properties (e.g. magnetism and electric conductivity) and structural characteristics. Several oxovanadium(IV) complexes with tetradentate Schiff base ligands, such as [VO(salpn)] (H_2salpn = *N,N′*-disalicylidene-1,3-propanediamine), have linear-chain structures (···V=O···V=O···) in the solid state.[1] It has been reported that these polymeric oxovanadium(IV) complexes with a $(d_{xy})^1$ electron configuration (z axis oriented along the V=O bond) have an intermolecular ferromagnetic interaction in the chains with an exchange coupling parameter, $J \approx +5\ cm^{-1}$.[2,3] The occurrence of a ferromagnetic interaction for these complexes has been explained in terms of McConnell′s spin polarization theorem.[2]

Recently, the preparation of a polymeric nitridomanganese(V) complex [MnN(salpn)], by photoirradiation of an azidomanganese(III) complex has been reported.[4] The diamagnetic polymeric nitridomanganese(V) complex with a $(d_{xy})^2$ electron configuration has ···Mn≡N···Mn≡N··· chains in the crystal. This result led us to prepare a polymeric nitridochromium(V) complex with a $(d_{xy})^1$ electron configuration. All the polymeric nitridometal complexes (···M≡N···M≡N···) reported so far are diamagnetic with a d^0 (V^{V},[5,6] Mo^{VI},[7] W^{VI},[8] Re^{VII} [9]) or a d^2 (Mn^{V} [4]) electron configuration. This paper reports the first preparation and crystal structure of a polymeric nitridochromium(V) complex [CrN(salpn)]. The temperature dependence of magnetic susceptibilities and low-temperature magnetization experiments are also reported.

Results and Discussion

Synthesis

The starting chromium(III) complex $\{(CH_3)_2NH_2\}_2$-$[CrCl_2(salpn)]Cl$ (**1**) was prepared by the reaction of the Schiff base ligand with anhydrous chromium(III) chloride in DMF.[10] The dimethylammonium cation in **1** originates from the decomposition of DMF. The azidochromium(III) complex $(CH_3)_2NH_2[Cr(N_3)_2(salpn)]$ (**2**) was prepared by the reaction of **1** with sodium azide in acetone. The nitridochromium(V) complex [CrN(salpn)] (**3**) was prepared by photoirradiation of **2** in acetonitrile. The orange complex **3** is stable in air at ambient temperature. The IR spectrum of **3** shows the Cr≡N stretching bands at 956 and 961 cm^{-1}, which are significantly shifted to lower energy than that of monomeric [CrN(salen)] (1012 cm^{-1}).[11] The electronic spectrum of **3** in acetonitrile shows a d−d transition band around 569 nm as a shoulder. This d−d band is assigned to the $3d_{yz,zx} \leftarrow 3d_{xy}$ transition, which is observed at 535 nm in the spectrum of [CrN(salen)].[12]

X-ray Crystal Structures

X-ray structure analyses of **1** and **3** were carried out. The molecular structures of **1** and **3** are shown in Figure 1 and 2, respectively. Selected bond lengths and angles are listed in Table 1 and 2, respectively.

Complex **1** has an octahedral structure with the chloro ligands in the *trans* position. The dimethylammonium cations are hydrogen bonded to the oxygen atoms of the ligand and the chloride ion [Figure 1(b)]. The distances N26···O4, N26···O5, N27···O4, N27···O5 are in the range 2.972(2)−3.151(2) Å, and the distances N26···Cl25 and N27···Cl25 are 3.140(2) Å and 3.151(2) Å, respectively. Prismatic crystals of **1** show dichroism; the (1 −1 0), (−1 1 0),

---

[a] Department of Chemistry, Faculty of Science and Technology, Keio University,
Hiyoshi 3−14−1, Kohoku-ku, Yokohama 223−8522, Japan
Fax: (internat.) +81-45/566-1697
E-mail: tmoto@chem.keio.ac.jp; ohba@chem.keio.ac.jp

[b] Department of Applied Chemistry, Faculty of Science and Technology, Keio University,
Hiyoshi 3−14−1, Kohoku-ku, Yokohama 223−8522, Japan
Fax: (internat.) +81-45/566-1551
E-mail: yoshioka@applc.keio.ac.jp

1434−1948/01/0404−1045 $ 17.50+.50/0

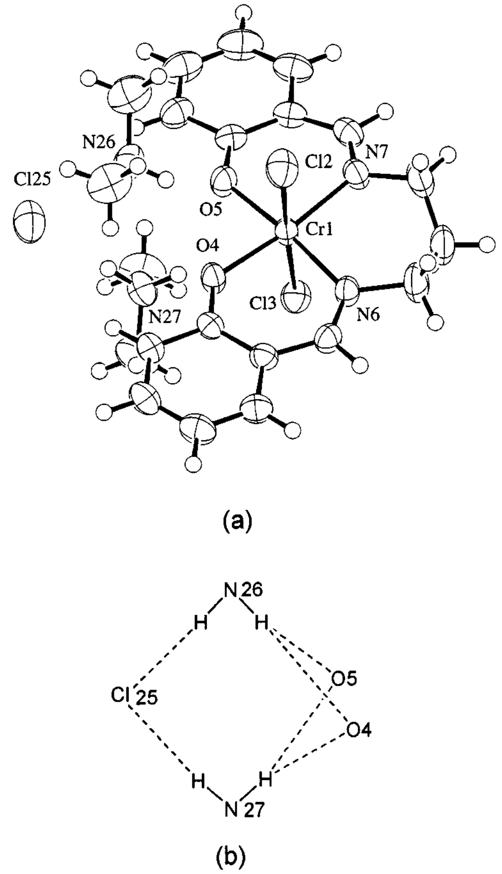

Figure 1. (a) ORTEP drawing of **1** with 50% probability ellipsoids; (b) schematic drawing of the hydrogen bonding in **1**

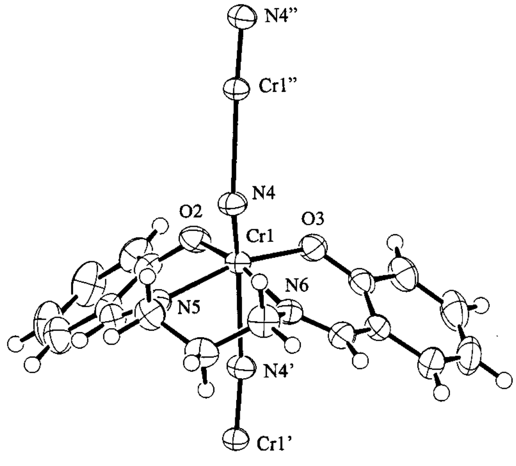

Figure 2. ORTEP drawing of **3** with 50% probability ellipsoids

(−1 0 1), (1 0 −1) planes are green, and the (1 1 0), (−1 −1 0) planes are brown.

Complex **3** has a polymeric structure with a distorted octahedral coordination geometry. The linear ···Cr≡N···Cr≡N··· chains run along the 2_1 screw axes parallel to the *c* axis. The Cr≡N and Cr···N distances are 1.559(2) Å and 2.508(2) Å, respectively. The Cr≡N···Cr angle is 153.7(1)°. The Cr1 atom is displaced by 0.321(1) Å from the N_2O_2 coordination plane. The six-membered N−N chelate ring shows a chair conformation. The crystal structure of **3** is isostructural with that of polymeric [MnN(salpn)], whose Mn≡N and Mn···N distances are 1.520(3) Å and 2.528(3) Å, respectively.[4] On the other hand, the V···O distance in polymeric [VO(salpn)] [2.213(9) Å][1] is shorter than the Cr···N distance in **3**. The V=O units in [VO(salpn)] are more strongly bonded to each other than the Cr≡N units in **3**.

Table 1. Selected bond lengths (Å) and angles (deg) of **1**

Cr1−Cl2	2.3615(6)	Cr1−Cl3	2.3522(6)
Cr1−O4	1.948(1)	Cr1−O5	1.946(1)
Cr1−N6	2.068(1)	Cr1−N7	2.052(2)
Cl2−Cr1−Cl3	176.66(2)	Cl2−Cr1−O4	89.88(4)
Cl2−Cr1−O5	92.73(4)	Cl2−Cr1−N6	89.46(4)
Cl2−Cr1−N7	89.16(4)	Cl3−Cr1−O4	90.81(4)
Cl3−Cr1−O5	90.59(4)	Cl3−Cr1−N6	87.25(4)
Cl3−Cr1−N7	90.54(4)	O4−Cr1−O5	83.26(5)
O4−Cr1−N6	91.74(6)	O4−Cr1−N7	173.09(6)
O5−Cr1−N6	174.53(6)	O5−Cr1−N7	89.96(6)
N6−Cr1−N7	95.09(6)		

Table 2. Selected bond lengths (Å) and angles (deg) of **3**[a]

Cr1−O2	1.934(2)	Cr1−O3	1.932(2)
Cr1−N4	1.559(2)	Cr1−N5	2.048(2)
Cr1−N6	2.039(2)	Cr1−N4′	2.508(2)
O2−Cr1−O3	85.85(9)	O2−Cr1−N4	102.7(1)
O2−Cr1−N5	88.49(9)	O2−Cr1−N6	161.11(9)
O3−Cr1−N4	102.7(1)	O3−Cr1−N5	161.27(9)
O3−Cr1−N6	88.43(9)	N4−Cr1−N5	96.0(1)
N4−Cr1−N6	96.1(1)	N5−Cr1−N6	91.23(9)
N4−Cr1−N4′	169.87(5)	Cr1−N4′−Cr1′	153.7(1)

[a] Primed atoms are generated by 1/2 − x, −y, 1/2 + z.

Magnetic Properties

The ESR spectrum of **3** in benzene at room temperature is shown in Figure 3. The spectrum shows a strong isotropic ESR signal due to the chromium isotope with $I = 0$ at $g_{\mathrm{iso}} = 1.978$, with a satellite quartet pattern ascribed to the less-abundant (9.5%) ^{53}Cr isotope with $I = 3/2$. The central strong signal and low-field satellite signals show a well-resolved septet superhyperfine structure [A(N) = 0.26 mT] with an intensity ratio of 1:3:6:7:6:3:1 due to three equivalent nitrogen nuclei, two from the salpn ligand and one

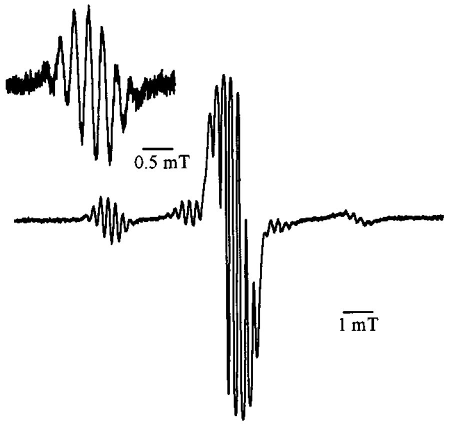

Figure 3. ESR spectrum of **3** in benzene at room temperature

from the apical nitrido atom. A similar extent of the Fermi-contact interaction occurs for the three nitrogen nuclei, despite their chemical nonequivalence. The equivalent isotropic superhyperfine coupling constants for the apical nitrido atom and the basal nitrogen atom are observed for [CrN(salen)][12] and other nitridochromium(V) complexes with tetradentate ligands.[13–15] The superhyperfine coupling constant (0.26 mT) in the spectrum of [CrN(salpn)] corresponds to a spin density of 0.005 on each nitrogen, based on the value of an isolated nitrogen atom (55.7 mT).[16]

The magnetic susceptibility data for **3**, plotted as the thermal variation of reciprocal molar susceptibility χ_m^{-1}, and $\chi_m T$, are shown in Figure 4 and 5, respectively. The behavior of the χ_m^{-1} vs. T plots in Figure 4 is well described by the Curie-Weiss law, $\chi_m = C/(T - \theta)$, with $C = 0.367$ emu K/mol and $\theta = +5.9$ K above 14 K. The positive θ value indicates the ferromagnetic interaction between the nitridochromium(V) spin centers. The overall appearance of the $\chi_m T$ vs. T plots in Figure 5 also indicates a ferromagnetic interaction. Although the $\chi_m T$ plots at 5000 G (represented as circles) show saturation below 5 K, the $\chi_m T$ value at 200 G (represented as triangles) increases even near T = 1.8 K. The magnetic susceptibility data can be analyzed using the Heisenberg model with the exchange interaction between the nitridochromium(V) ion on a chain [Equation (1)].

$$H = -J\sum_{i=1}^{n-1} S_i \cdot S_{i+1} \tag{1}$$

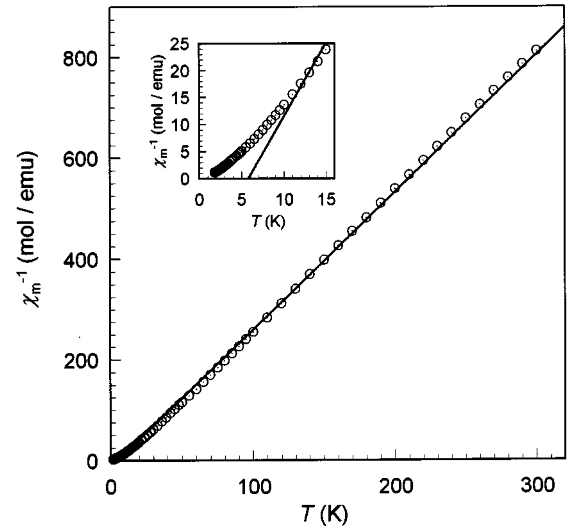

Figure 4. χ_m^{-1} vs. T (○) plot of **3**; the inset shows the χ_m^{-1} vs. T plot in the low-temperature region; the solid lines were calculated from the Curie-Weiss law

The thermal variation of magnetic susceptibility of a magnetic chain can be described by the empirical function introduced by Baker et al. [Equation (2)].[17]

$$\chi_m = \frac{N_A g^2 \beta^2}{kT} F(J,T)$$

with

$$F(J,T) = \frac{1}{4}[(1 + 5.7979916x + 16.902653x^2 + 29.376885x^3 + 29.832959x^4 + 14.036918x^5)/(1 + 2.7979916x + 7.0086780x^2 + 8.6538644x^3 + 4.5743114x^4)]^{2/3} \tag{2}$$

and

$$x = \frac{J}{2kT}$$

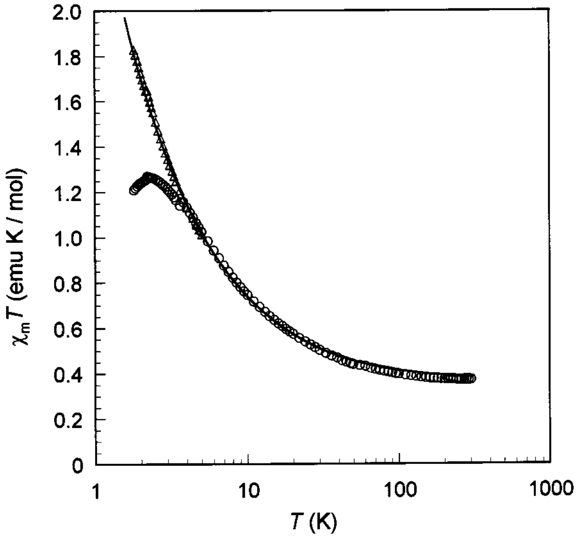

Figure 5. $\chi_m T$ vs. T plots of **3** under an applied field of 0.02 T (△) and 0.50 T (○)

The best-fit curve using Equation (2) is shown as a solid line in Figure 5, corresponding to $J = +8.4$ cm^{-1}. To clarify the intermolecular coupling, the magnetization of **3** was measured at 1.8 K (Figure 6). The magnetization curve of **3** exceeds the Brillouin function with $S = 1/2$ and nearly coincides with that of $S = 12/2$ at 1.8 K, indicating the formation of a high-spin cluster with $S = 12/2$ on average.

According to the McConnell theorem,[18] the exchange interaction between two aromatic radicals A and B can be described by the sum of the two-center exchange integrals in the form

$$H^{AB} = -S^A \cdot S^B \sum_{ij} J_{ij}^{AB} \rho_i^A \rho_j^B \tag{3}$$

where S^A and S^B are the total spin operators for molecules A and B, respectively, and ρ_i^A and ρ_j^B are the π-spin densities on atoms i and j of A and B, respectively. If we apply Equation (3) to a dimer of nitridochromium(V) units (each is denoted as A and B) in **3**, and consider that i and j correspond to the chromium(V) ion and the nitrido ion, respectively, Equation (3) can be written in the form

$$H^{AB} = -S^A \cdot S^B J_{\mathrm{Cr \cdots N}}^{AB} \rho_{\mathrm{Cr}}^A \rho_{\mathrm{N}}^B \tag{4}$$

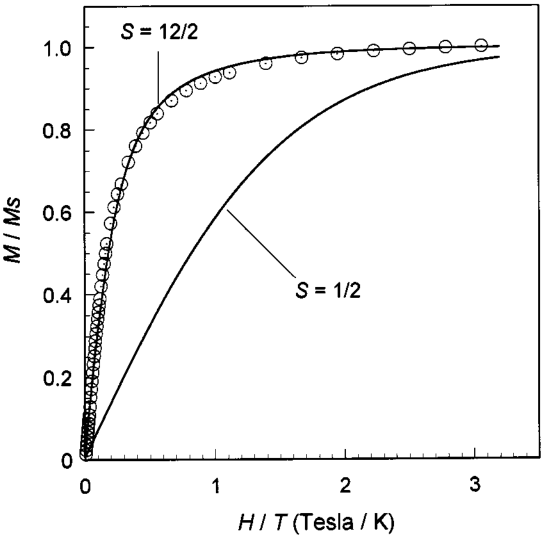

Figure 6. Magnetization isotherm of **3** at 1.8 K; the solid lines were calculated with the Brillouin function

When a ferromagnetic intermolecular coupling is observed between molecules A and B, $J^{AB}_{Cr\cdots N}$ is negative and ρ^{A}_{Cr} and ρ^{B}_{N} are positive and negative, respectively. Spin polarization on the nitrido ion was observed in the ESR spectrum of **3**, although the sign of the polarized spin is uncertain. A negative spin density is expected for the polarized spin on the nitrido ion.

In the present study, a ferromagnetic intermolecular interaction between the nitridochromium(V) spin centers is observed for **3**. A similar ferromagnetic intermolecular interaction is observed for polymeric [VO(salpn)] with the same $(d_{xy})^1$ electronic configuration. However, the magnetic interaction in **3** ($J = +8.4$ cm^{-1}) is larger than that in [VO(salpn)] ($J = +5.2$ cm^{-1}),[2] while the distance between the Cr≡N units in **3** is longer than that between the V=O units in [VO(salpn)] (vide supra). Further investigations are necessary to elucidate the intermolecular ferromagnetic coupling in the Cr≡N and V=O polymeric systems.

Experimental Section

$\{(CH_3)_2NH_2\}_2$[CrCl$_2$(salpn)]Cl (1): The ligand H$_2$salpn was prepared by the reaction of 1,3-propanediamine with two equivalent amounts of salicylaldehyde in ethanol. The solvent was evaporated from the reaction mixture to yield an oily product, which was used for the following reaction without purification. To a DMF solution (300 mL) of the ligand (50 mmol), was added anhydrous chromium(III) chloride (7.92 g, 50 mmol). The reaction mixture was refluxed for 4 h. After cooling, unreacted chromium(III) chloride was removed by filtration, and the filtrate was evaporated to dryness. The residue was suspended in ethanol, and the precipitate was collected by filtration. The light green powder was washed with ethanol and ether, and dried. Yield: 18.1 g (68%). − $C_{21}H_{32}Cl_3Cr_1N_4O_2$ (530.86): calcd. C 47.51, H 6.08, N 10.55; found C 47.56, H 6.10, N 10.54.

$(CH_3)_2NH_2$[Cr(N$_3$)$_2$(salpn)] (2): To a suspension of $\{(CH_3)_2NH_2\}_2$[CrCl$_2$(salpn)]Cl (8.0 g, 15 mmol) in acetone (1 L), was added sodium azide (2.6 g, 40 mmol). The mixture was refluxed for 3 h, and filtered. The green precipitate was dissolved in hot acetone (2 L), and insoluble salts were removed by filtration. The combined filtrate was evaporated to dryness, and the residue was suspended in diethyl ether. A green crude product was collected by filtration and dried. Yield: 6.6 g (96%). IR (KBr): $\tilde{\nu}$ = 2058 cm^{-1} $\nu(N_3)$. The complex was used for the following reaction without purification.

[CrN(salpn)] (3): Although no problems were encountered in this study, azide complexes are explosive and photolysis of the complex was carried out with caution. $(CH_3)_2NH_2$ [Cr(N$_3$)$_2$(salpn)] (1.39 g, 3 mmol) was suspended in acetonitrile (1 L), and the mixture was irradiated with a 400 W high-pressure mercury lamp below 20 °C under an argon atmosphere, with stirring. After 2 h, another 3 mmol of the azido complex was added to the reaction mixture, and the mixture was irradiated for 24 h. The color of the mixture gradually turned to red during the irradiation. After irradiation, the mixture was filtered, and the filtrate was evaporated to ca. 5 mL. The resulting orange precipitate was collected by filtration, and dried. This crude product was dissolved in dichloromethane, and applied to a silica gel column (∅ 3.5 cm × 20 cm). The product was eluted with dichloromethane/ethyl acetate (10:1 v/v). A main orange band was collected and evaporated to dryness to yield orange needle crystals. Yield: 1.12 g (54%). − $C_{17}H_{16}Cr_1N_3O_2$ (346.33): calcd. C 58.96, H 4.66, N 12.13; found C 58.83, H 4.66, N 12.09. − IR (KBr): $\tilde{\nu}$ = 956 cm^{-1}, 961 ν(Cr≡N). − UV/Vis {CH$_3$CN, $\sigma/10^3$ cm^{-1} (log ε/M^{-1}cm^{-1})}: λ = 17.6 (1.70, sh), 21.7 (sh), 27.0(3.87), 36.0 (4.37), 41.2 (4.69).

X-ray Crystallographic Study: Dichroic (green and brown) prismatic crystals of $\{(CH_3)_2NH_2\}_2$[CrCl$_2$(salpn)]Cl (**1**) were obtained by slow diffusion of diethyl ether vapor into a DMF solution of the complex. Orange needle crystals of [CrN(salpn)] (**3**) were grown from a dichloromethane solution. The intensity data were collected at 25 °C on a Rigaku four-circle AFC-7R diffractometer with graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å) up to $2\theta = 55°$ by $\theta-2\theta$ scans. Three standard reflections were measured at every 150 reflections. Absorption corrections were made by the numerical integration method for **1**,[19] and the Ψ scans method for **3**.[20] The structures were solved by direct methods on a Silicon Graphics O^2 workstation with the program system TEXSAN.[21] Non-hydrogen atoms were treated anisotropically, and hydrogen atoms were introduced at ideal positions. Refinement was based on F^2 against all the 5837 reflections for **1**, and against 2062 reflections for **3**. The R value was 0.031 for the 4912 reflections with $I > 2\sigma(I)$ for **1**, and 0.029 for 1780 reflections with $I > 2\sigma(I)$ for **3**. The absolute structure of **3** was determined with the Flack parameter $x = -0.05(3)$.[22] The crystal data and experimental details are listed in Table 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-148481 (**1**) and -148482 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Magnetic Measurements: The magnetic susceptibility measurements were carried out with a SQUID magnetometer (Quantum Design MPMS-5) in the temperature range 1.8−300 K using a magnetic field of 0.5 and 0.02 T. The susceptibilities of **3** have been corrected for the diamagnetic contribution of $\chi_{dia} = -166 \times 10^{-6}$ emu mol^{-1}, calculated by Pascal's method. Magnetization experiments up to 5.5 T were carried out at 1.8 K.

Table 3. Crystallographic Data for **1** and **3**

	1	**3**
Formula	$C_{21}H_{32}Cl_3Cr_1N_4O_2$	$C_{17}H_{16}Cr_1N_3O_2$
Fw	530.9	346.3
Crystal size, mm	0.50 × 0.40 × 0.15	0.55 × 0.10 × 0.10
Space group	$P\bar{1}$	$P2_12_12_1$
a, Å	10.810(2)	11.670(3)
b, Å	11.362(1)	16.785(2)
c, Å	10.736(2)	7.928(3)
α, °	92.90(1)	90
β, °	103.56(2)	90
γ, °	94.95(1)	90
V, Å^3	1273.7(3)	1553.0(6)
Z	2	4
ρ_{calc}, g/cm^3	1.384	1.481
μ, mm^{-1}	0.788	0.750
λ, Å	0.71073	0.71073
T, °C	25	25
R[a]	0.031	0.029
R_w[b]	0.090	0.080

[a] $[\Sigma(F_o^2 - F_c^2)^2/\Sigma w(F_o)^2]^{1/2}$. – [b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (0.0445P)^2 + 0.4789P$ for **1** and $R_w = [\Sigma w\ (F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (0.0446P)^2 + 0.2606P$ for **3**, where $P = (F_o^2 + 2F_c^2)/3$.

Other Measurements: IR spectra were recorded on a JASCO A-202 spectrophotometer. The electronic spectrum was recorded on a JASCO V-570 spectrophotometer. The ESR spectrum in benzene at room temperature was recorded on a JEOL JES-RE3X spectrometer with a 100 kHz field modulation.

---

[1] M. Mathew, A. J. Carty, G. J. Palenik, *J. Am. Chem. Soc.* **1970**, *92*, 3197–3198.
[2] M. Tsuchimoto, N. Yoshioka, *Chem. Phys. Lett.* **1998**, *297*, 115–120.
[3] R. F. Drake, V. H. Crawford, W. E. Hatfield, G. D. Simpson, G. O. Carlisle, *J. Inorg. Nucl. Chem.* **1975**, *37*, 291–293.
[4] M. Tsuchimoto, H. Iwamoto, M. Kojima, S. Ohba, *Chem. Lett.* **2000**, 1156 –1157.
[5] W. Willing, R. Christophersen, U. Müller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1987**, *555*, 16–22.
[6] S. C. Critchlow, M. E. Lerchen, R. C. Smith, N. M. Doherty, *J. Am. Chem. Soc.* **1988**, *110*, 8071–8075.
[7] D. M. -T. Chan, M. H. Chisholm, K. Folting, J. C. Huffman, N. S. Marchant, *Inorg. Chem.* **1986**, *25*, 4170–4174.
[8] M. H. Chisholm, D. M. Hoffman, J. C. Huffman, *Inorg. Chem.* **1983**, *22*, 2903–2906.
[9] W. Liese, K. Dehnicke, I. Walker, J. Strähle, *Z. Naturforsch* **1979**, *34B*, 693–696.
[10] C. M. Che, J. X. Ma, W. T. Wong, T. F. Lai, C. K. Poon, *Inorg. Chem.* **1988**, *27*, 2547–2548.
[11] S. I. Arshankow, A. L. Poznjak, *Z. Anorg. Allg. Chem.* **1981**, *481*, 201–206.
[12] N. Azuma, Y. Imori, H. Yoshida, K. Tajima, Y. Li, J. Yamauchi, *Inorg. Chim. Acta* **1997**, *266*, 29–36.
[13] J. W. Buchler, C. Dreher, K.-L. Lay, A. Raap, K. Gersonde, *Inorg. Chem.* **1983**, *22*, 879–884.
[14] J. T. Groves, T. Takahashi, W. M. Butler, *Inorg. Chem.* **1983**, *22*, 884–887.
[15] N. Azuma, T. Ozawa, S. Tsuboyama, *J. Chem. Soc., Dalton Trans.* **1994**, 2609–2613.
[16] B. A. Goodman, J. B. Raynor, *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 135–362.
[17] G. H. Baker, Jr., G. S. Rushbrooke, H. E. Gilbert, *Phys. Rev. A* **1964**, *135*, 1272–1277.
[18] H. M. McConnell, *J. Chem. Phys.* **1963**, *39*, 1910.
[19] P. Coppens, L. Leiserowitz, D. Rabinovich, *Acta Cryst.* **1965**, *18*, 1035–1038.
[20] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Cryst.* **1968**, *A24*, 351–359.
[21] TEXSAN, Version 1.9, Single crystal structure analysis software, MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, U.S.A and Rigaku, 3-9-12 Akishima, Tokyo, Japan.
[22] H. D. Flack, *Acta Cryst.* **1983**, *A39*, 876–881.

Received August 25, 2000
[I00328]