

Contribution from the Institut für Theoretische Chemie der Universität Düsseldorf,
D-4000 Düsseldorf, Federal Republic of Germany

The Cyanate Ion as Bridging Ligand: Synthesis, Spectroscopic Characterization, and Magnetic Properties of (μ -Cyanato)bis(pentaamminechromium(III)) Chloride

Thomas Schönherr

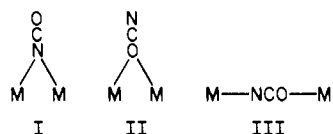
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The first cyanato-bridged chromium complex and its deuterated analogue have been prepared by thermal decomposition of urea in the presence of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. With the aid of vibrational analysis the bridging has been determined to be end-to-end, including a hitherto unknown Cr-OCN bonding unit. The visible-ultraviolet absorption spectrum can be assigned to single ions in tetragonally distorted environments by using conventional ligand field theory. Magnetic susceptibility data have been interpreted in terms of a weak antiferromagnetic coupling, yielding a value of -0.4 cm^{-1} for the exchange integral J , which corresponds to a singlet-triplet separation of 0.8 cm^{-1} . Considering the various possible exchange pathways, little deviation from linearity in the Cr-NCO-Cr bonding unit is expected.

Introduction

The ligand behavior of the cyanate ion (NCO^-) is of interest because of its potential ambidentate character. Contrary to the situation with the pseudohalides NCS^- and NCSe^- , which have been studied in more detail,¹ only one pair of linkage isomers has been reported, which are characterized by different positions and intensities of their infrared peaks.² Furthermore the cyanate ion is commonly N-bonded,³⁻⁶ which has often been explained in terms of a small charge density on the cyanate oxygen atom;⁷ INDO calculations, however, have shown that almost equal electron densities exist at nitrogen and oxygen.⁸ Nevertheless, unlike those of heavier metal ions, almost all cyanate complexes of first-row transition metals have been claimed to be N-bonded, and the only authenticated case of a metal-OCN bonding was found for a bis(μ -cyanato)nickel dimer.⁹

Preparations of cyanate complexes in aqueous media are complicated by rapid hydrolysis processes. To avoid such reactions, (isocyanato)pentaamminechromium(III) has been synthesized by thermal decomposition of urea in the presence of chromium(III) ions.³ This reaction, which may be considered as a reversal of Wöhler's synthesis, is catalyzed by certain metal ions. This work reports the preparation of the title compound by the reaction of molten urea with $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ yielding the first example of a binuclear molecule with a single cyanato bridge. The existence of this dimeric complex had been supposed earlier^{10,11} and is now unequivocally shown by the magnetic behavior of this compound, which exhibits an antiferromagnetic exchange coupling between the paramagnetic centers. The geometry of the complex is discussed in terms of three possible bridging modes for single-bridged cyanate dimers:



The tendency of the cyanate group to bridge via its nitrogen atom is known; e.g., zigzag Ag-N-Ag chains with a bond angle of 128° have been found.¹² Bridging via cyanate oxygen is still

unknown, in contrast to many thiocyanate compounds that exhibit S-bonded dimeric units.¹ The type of bonding influences the charge distribution and bond orders within the NCO^- group, leading to characteristic frequency shifts in the infrared spectra.^{13,14} Calculations have supported the experimental findings, which in most cases indicate strong preference for metal-NCO bonding.^{15,16} If these results are compared with the present observed infrared shifts, the end-to-end structure (III) has to be assumed for the present chromium(III) cyanate dimer.

Exchange coupling between paramagnetic ions can be described by the familiar isotropic HDVV-Hamiltonian¹⁷

$$H_{\text{ex}} = -2JS_a S_b - j(S_a S_b)^2 \quad (1)$$

when the single-ion ground state is an orbital singlet. The coupling parameters J and j represent the bilinear and biquadratic interdimer interaction ($j \ll J$) between chromium ions with the spin operators S_a and S_b . Eigenvalues of H_{ex} yield a manifold of spin levels having $S = 0, 1, 2, 3$, with the $S = 0$ state lowest in energy if the interaction is antiferromagnetic in nature ($J < 0$). Ferromagnetic interactions ($S = 3$ ground state, $J > 0$), resulting from parallel aligned spins in the ground state, are fairly rare for chromium(III) dimers.¹⁸ Magnetic susceptibility data from the present binuclear complex can be fitted, neglecting j , with the more simple Hamiltonian

$$H_{\text{ex}} = -2JS_a S_b + g\mu H_z \quad (2)$$

and weak antiferromagnetism is observed.

Experimental Section

(a) Synthesis. $[(\text{NH}_3)_5\text{Cr}(\text{NCO})\text{Cr}(\text{NH}_3)_5]\text{Cl}_3$. A mixture of equal amounts of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and urea was placed in an open flask and heated at 120°C . When most of the water of hydration disappeared, the temperature was raised to 170°C and maintained for 24 h. The residue was stirred in boiling methanol, filtered, and washed successively with ice-cold water, methanol, and ether. The pink product was dried and stored in the dark. Yield: 80%. Further purification by recrystallization was not possible since the compound is insoluble in common organic solvents and decomposition occurs rapidly in the presence of water. Thus the binuclear complex was not separated completely from small amounts of monomeric impurities, and crystals suitable for X-ray measurements could not be obtained.

$[(\text{ND}_3)_5\text{Cr}(\text{NCO})\text{Cr}(\text{ND}_3)_5]\text{Cl}_3$ was synthesized by the same technique using deuterated urea (VEB Berlin-Chemie, 97.5% D) and $\text{CrCl}_3 \cdot n\text{D}_2\text{O}$ as starting materials.

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$[\text{Cr}(\text{NH}_3)_5(\text{NCO})]\text{Cl}_2$ was prepared from the nitrate salt as described previously.³ It was also obtained by alkaline hydrolysis of the binuclear complex (see text).

(b) **Physical Measurements.** Infrared spectra in the 4000–500- cm^{-1} range were taken by the KBr pellet technique on a Perkin-Elmer 325 IR spectrometer. The integrated intensities of IR absorption were calculated in analogy to Ramsey's method of direct integration.¹⁹ Far-infrared spectra for polyethylene pellets were recorded on a Beckman 720 Fourier spectrometer equipped with an evacuable sample chamber of our own design, avoiding additional windows for the cryostat.²⁰

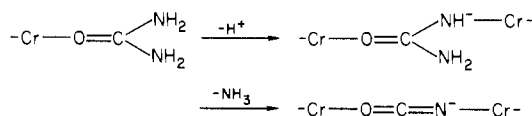
Raman measurements were carried out on an apparatus previously described, with some modifications to the optical train.²⁰ Although various excitation lines were used, reproducible Raman spectra could not be obtained, since decomposition occurred rapidly even at liquid-helium temperatures, due to the high absorptivity of the compound in the argon laser spectral region. To overcome these problems a spinning sample holder and longer wavelength excitation would be required.

Visible-ultraviolet spectra of aqueous solutions were obtained by standard methods. Spin-forbidden transitions were recorded on Nujol mulls at liquid-helium temperatures by using the facilities mentioned above.

Magnetic susceptibility measurements were kindly performed by W. Haase and H. Astheimer, Technische Hochschule Darmstadt, using Faraday's method. The apparatus is described elsewhere.²¹

Results and Discussion

(a) **Formation of the Chromium–Cyanate Bonds.** Reaction of urea with chromium(III) salts in aqueous solutions yields O-bonded hexakis(urea)chromium(III), which can be readily isolated from the heated mixture (120 °C). At temperatures above ca. 150 °C, urea decomposes to ammonia and isocyanic acid in the presence of certain metal ions, and various ammine complexes are formed. When nickel(II) salts are used, this reaction was found to yield the hexaammine complex, whereas in the presence of chromium ions, pentaammines are synthesized that involve quite unexpected cyanate ligands. For the reaction pathway that leads to the cyanate bridging unit, a reaction mechanism without cleavage of the Cr–O bond is assumed:



This description is at variance with Balahura,⁵ who explained the formation of $[\text{Co}(\text{NH}_3)_5\text{NCO}]^{2+}$ in terms of an intermediate N-bonded urea complex. But the fact that cobalt and chromium urea complexes are O-bonded and linkage isomerism is not observed in solution or in the solid state favors the reaction pathway presented here, even for the synthesis of the monomeric species by formation of a transient binuclear complex.³

(b) **Hydrolysis Properties.** Kinetics of acid-catalyzed hydrolysis have been studied for several isocyanatopentaammines, and it has been found that this reaction generally leads to formation of hexaammine complexes in high yield.^{5,22,23} In the case of the binuclear chromium cyanate complex, several products, characterized by absorption spectra and in part by IR frequencies, can be obtained, depending on the acid employed.

(i) Treatment with 6 M perchloric acid produces almost quantitatively the very insoluble $[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{ClO}_4)_3$, which is not obtained by identical treatment of the monomeric $[\text{Cr}(\text{NH}_3)_5(\text{NCO})]^{2+}$ complex.²³

(ii) Pink to violet solutions are formed when the dimer reacts with 6 M nitric acid, as substitution of ammonia by water molecules occurs in a stepwise manner. From visible absorption spectra the most likely products are found to be di- and tri-ammines, and finally $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is obtained, characterized by absorption peaks at 574 and 407 nm.

(iii) No reaction in concentrated hydrochloric acid is observed, because of the insolubility of the chloride salt. The products

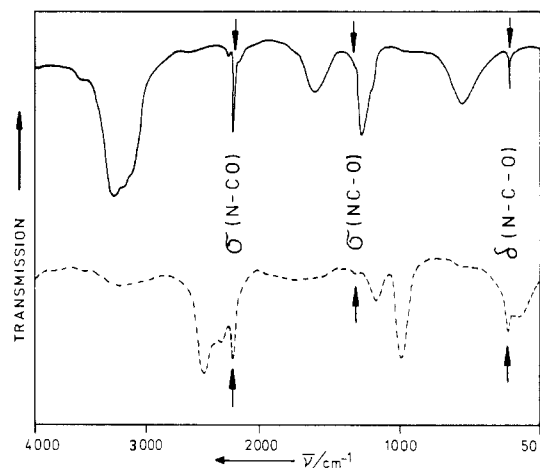


Figure 1. Infrared spectra of the μ -cyanato complex at 295 K. The spectrum of the deuterated compound is given by the broken line.

Table I. Vibrational Peaks and Assignments of the Undeuterated (H) and the Deuterated (D) Binuclear Complexes

$\bar{\nu}(\text{H}), \text{cm}^{-1}$	$\bar{\nu}(\text{D}), \text{cm}^{-1}$	$\bar{\nu}(\text{H})/\bar{\nu}(\text{D})$	assgnt
3270	2450	1.34	$\sigma_{\text{as}}(\text{NH}_3)$
3200	2380		
3140	2290		
2248	2244	1.00	$\sigma(\text{N-CO})$
1597	1175	1.36	$\delta_{\text{d}}(\text{NH}_3)$
1315	1303	1.01	$\sigma(\text{N-C-O})$
1288	995	1.29	$\delta_{\text{s}}(\text{NH}_3)$
760	590	1.29	$\delta(\text{Cr-N-H})$
605	607	0.99	$\delta(\text{N-C-O})$
472	430	1.09	$\sigma(\text{Cr-NH}_3)$
458	422		
438	408		
350	341	1.03	$\sigma(\text{Cr-NCO})$
303	297	1.02	$\sigma(\text{Cr-OCN})$
278	250	1.10	$\delta(\text{H}_3\text{N-Cr-NH}_3)$
248	226		
224	204		
186	192	0.97	$\delta(\text{Cr-N-C})$
164	168	0.98	$\delta(\text{Cr-O-C})$

obtained in dilute hydrochloric acid solutions are as described in (ii).

All reactions were performed at room temperature in the dark to prevent photolysis processes. Contrary to the situation with monomeric isocyanato complexes, no hexaammine is formed by the acid-catalyzed hydrolysis of the dimer. This indicates that in acid media decomposition of the complex begins with cleavage of the Cr–NCO bond. On the other hand, after treatment of the chromium cyanate dimer with 2 M sodium hydroxide solution for 24 h, the orange (isocyanato)pentaamminechromium(III), is obtained as a residue in a solution containing primarily hydroxopentaamminechromium(III). Thus alkaline hydrolysis leads to Cr–OCN bond rupture whereas cleavage of the Cr–NCO bonding unit is preferentially catalyzed in acids. This demonstrates the expected weaker acidity of cyanate nitrogen compared to cyanate oxygen.

(c) **Vibrational Structure.** Infrared spectroscopy has been widely used to establish the mode of bonding in complexes containing chalcogenate groups. Figure 1 shows the room-temperature IR spectra of the deuterated and undeuterated dimer in the region 4000–500 cm^{-1} . The peaks obtained are compiled in Table I together with their band shifts on deuteration as given by the frequency relations. The band pattern closely resembles that of the (isocyanato)pentaamminechromium complex, therefore assignments can be made in correspondence with results from the vibrational analysis of the monomeric species.²⁰ Internal ammonia vibrations are located as several strong broad bands, which show very large deuterium shifts. Two sharp cyanate peaks are observed at 2248 and 605 cm^{-1} , which are assigned to $\sigma(\text{N-C})$ stretching and $\delta(\text{N-C-O})$ bending modes. The latter degenerate mode is

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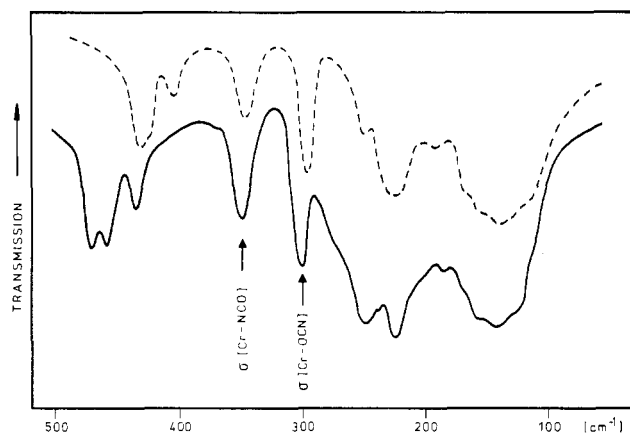
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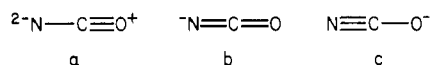
Table II. Vibrational Frequencies (cm^{-1}) of the NCO^- Group in Various Cyanates

	$\sigma(\text{N-CO})$	$\sigma(\text{NC-O})$	$\delta(\text{N-C-O})$	ref
NCO^-^a	2220	1305	620	42
$\text{Ag} \begin{cases} \text{NCO}^b \\ \text{NCO}^b \end{cases}$	2170	1350	657, 598	16
$[(\text{NH}_3)_3\text{Cr}(\text{NCO})](\text{NO}_3)_2$	2240	1315	605	20
$[(\text{NH}_3)_3\text{Cr}(\text{NCO})]\text{Cl}_2$	2242	1325	605	this work
$\cdots\text{Cr-NCO-Cr}\cdots$	2248	1315	605	this work

^a In sodium cyanate. ^b Part of the chain structure in silver cyanate.

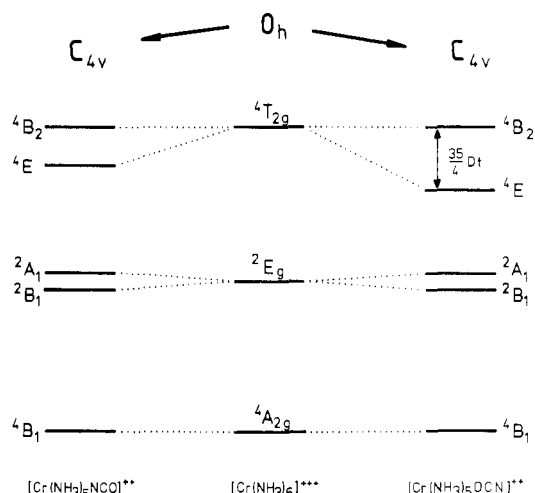
**Figure 2.** Far-infrared spectra of the μ -cyanato complex given as in Figure 1.

not split, reflecting a fairly high symmetry for the binuclear complex (vide infra). The C–O stretch is assigned to the very weak shoulder of the broad band at 1292 cm^{-1} , which can be distinguished from internal ammonia vibrations by frequency relations with respect to the deuterated sample. This assignment is less certain, since strong Fermi resonance with the first overtone of $\delta(\text{N-C-O})$ may occur.²⁴ In comparison with the vibrational frequencies of (isocyanato)pentaamminechromium(III), the cyanate bands of the binuclear complex are slightly shifted (Table II). This can be understood if the resonance structures of the cyanate ion are considered that make different contributions to force constants and vibrational frequencies:¹³



With respect to the N-bonded monomeric complex, resonance form a will become most important in the bridging case (I), whereas form c will increase when Cr–O bonds are formed. As calculated by Maki and Decius,¹⁴ $\sigma(\text{C-N})$ will be found at the lowest frequencies when the nitrogen atom is connected to two metal ions, as found in the AgNCO structure (case I). The positions of the IR bands attributable to the NCO^- group of various cyanate compounds are given in Table II. Since a small frequency shift to higher wavenumbers is observed in the dimer, it is reasonable to exclude the purely N-bonded case (I) for the present complex. As a further indication, the frequency of the C–O stretching mode is slightly lowered, although the uncertainty of this assignment must be considered.

The far-infrared spectra, where the metal–ligand stretching and bending vibrations are located, are shown in Figure 2. The peaks at 472 and 438 cm^{-1} are assigned to $\sigma(\text{Cr-NH}_3)$ stretching vibrations, and the splitting of the more prominent band is more likely explained by hydrogen bonding to the chloride ions²⁵ than by lack of symmetry. In the frequency region below 290 cm^{-1} , several angular vibrations can be distinguished from their different isotope shifts. Three peaks with shift quotients of about 1.1 are

**Figure 3.** Lowest quartet and doublet electronic states of d^3 ions in octahedral and tetragonal environments.

assigned to $\delta(\text{H}_3\text{N-Cr-NH}_3)$ bending modes, in good agreement with results from the monomeric isocyanate complex.²⁰ The weak bands at 186 and 164 cm^{-1} , which show almost no isotope effect, may be candidates for chromium cyanate bending vibrations, probably with decreasing energy for $\delta(\text{Cr-N-C})$ and $\delta(\text{Cr-O-C})$. This indicates the appearance of a Cr–OCN bond, which is strongly supported by the two intense bands at 350 and 298 cm^{-1} , which also exhibit very small isotope effects. From the vibrational analysis for $[\text{Cr}(\text{NH}_3)_5(\text{NCO})]^{2+}$, the 350-cm^{-1} peak can be readily assigned to the Cr–NCO stretch.²⁰ Therefore the solely O-bonded case II is eliminated too; thus an end-to-end structure has to be assumed for the cyanato-bridged complex (case III). This is nicely confirmed by the additional single band at 298 cm^{-1} , which most likely belongs to the Cr–OCN stretching vibration. This assignment is reasonable when compared with the vibrational energies of metal–O stretches observed in various amino acid chromium(III) complexes.^{26,27} The negligible deuteration shift of this band is emphasized, and furthermore this peak vanishes in the infrared spectra of alkaline hydrolysis products, when rupture of bridging bonds will preferentially occur between chromium and oxygen.

An additional method to determine the mode of chalcogeno-cyanate coordination involves the integrated intensity of the C–N stretching vibration in solution spectra.¹³ When KBr disks are used, several factors may affect the band shapes in an undetermined way; nevertheless, a general trend can be stated.¹ For the compounds under discussion the integrated intensity for the binuclear complex is about 3 times smaller than the value obtained for the monomeric isocyanate complex. In the former case resonance form c will increase, and the dipole moment over the C–N bond is decreased. Assuming that the rate of change of this dipole is affected in the same sense, a decrease in the intensity of the C–N vibration is expected. This has been experimentally manifested for an abundance of cyanate and thiocyanate complexes, where the highest intensities have been generally found for iso structures.^{1,13} Thus the lower intensity of the C–N stretch in the IR spectrum also supports the end-to-end structure of the binuclear complex.

(d) Electronic Transitions. Since exchange interaction between the two paramagnetic ions was found to be very weak (vide infra), the visible–ultraviolet spectrum of the dimer can be treated on the basis of two quasi-tetragonal fragments, each of them independently contributing to the observed band shape. The energy level scheme for tetragonal chromium(III) is well established and is displayed in Figure 3 for the lowest quartet and doublet states. The room-temperature spectra of freshly prepared solutions show two broad bands, centered at 19900 and 26600 cm^{-1} (Figure 4),

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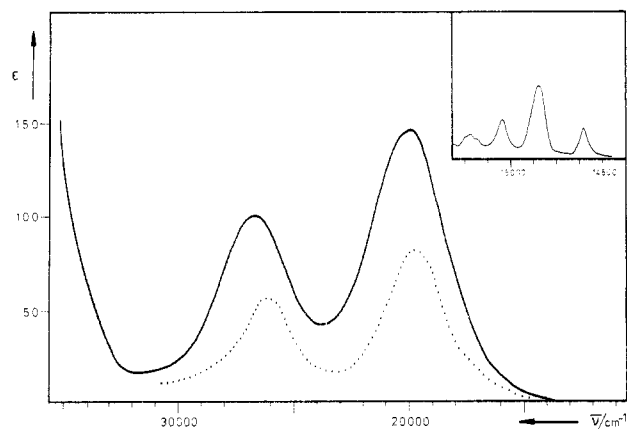


Figure 4. Absorption spectrum of the binuclear complex in aqueous solution at room temperature. The calculated hypothetical spectrum of $[\text{Cr}(\text{NH}_3)_5(\text{OCN})]^{2+}$ is displayed by the dotted line. The zero phonon region of the intercombination band spectrum at 10 K is given within the insert.

which are assigned to the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transitions (in O_h notation). Low-symmetry splitting of these quartet bands is not observed, as predicted by ligand field theory when ligands have similar positions in the spectrochemical series. Compared to that of the N-bonded isocyanato complex, the first spin-allowed band is shifted considerably to lower energy. This results from the smaller ligand field strength of the O-bonded chromophore and spectral shifts of such kind are well-known for linkage isomers of cyanate and thiocyanate complexes.^{2,28} If the spectrum of the (isocyanato)pentaamminechromium(III) is subtracted from the spectrum of the binuclear complex, the absorption band shape of the hypothetical O-bonded linkage isomer can be determined approximately (Figure 4). Since from theory the ${}^4B_2 (C_{4v})$ split level has to be located at the position of the first quartet band of the parent cubic hexaammine complex ($10Dq_{\text{NH}_3} = 21\,500 \text{ cm}^{-1}$), the calculated maximum at $19\,700 \text{ cm}^{-1}$ represents the transition ${}^4B_1 (C_{4v}) \rightarrow {}^4E (C_{4v})$, which usually exhibits higher intensities in tetragonal chromium(III) complexes. Ligand field theory predicts that the observed splitting of ${}^4T_{2g} (O_h)$ depends only on the axial parameter Dt when configuration interaction is neglected:

$$-{}^{35}/_4Dt = \Delta E[{}^4B_2 - {}^4E] \quad (3)$$

Hence, a value of ca. -200 cm^{-1} is obtained for Dt , which may be used in the following relation adequate for monosubstituted complexes:²⁹

$$Dt = -{}^{27}/_7[Dq_{\text{NH}_3} - Dq_{\text{OCN}^-}] \quad (4)$$

From this the magnitude of Dq_{OCN^-} is very approximately calculated to be 1450 cm^{-1} . This is in quite good agreement with values for other O-bonded ligands, and the position of the cyanate group in the spectrochemical series is established between urea ($Dq = 1600 \text{ cm}^{-1}$) and chloride ($Dq = 1380 \text{ cm}^{-1}$).

The intercombination band region is characterized by three strong peaks at $14\,683$, $14\,879$, and $15\,035 \text{ cm}^{-1}$ (Figure 4). Temperature-dependent measurements do not show any remarkable intensity changes or frequency shifts as have been observed for several hydroxo-bridged chromium(III) dimers.^{30,31} Therefore these bands cannot be explained as a splitting pattern of magnetically coupled ground states in accordance with the observed weak antiferromagnetism, even if larger energy splittings of the 2E_g ${}^2E_g (O_h)$ pair states are possible.³¹ Thus these bands are tentatively assigned to zero phonon lines belonging to ${}^4A_{2g} (O_h) \rightarrow {}^2E_g (O_h)$ transitions of the single ions, split by the actual

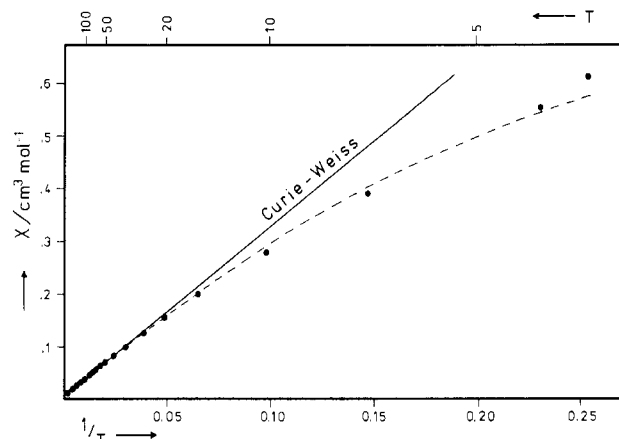


Figure 5. Experimental (•••) and calculated (---) magnetic susceptibilities of the μ -cyanato-bridged chromium(III) dimer.

lower symmetry, which usually exhibit the highest intensities in vibronic spectra of tetragonal chromium(III) complexes.^{27,32} In total, four pure electronic transitions are expected in C_{4v} symmetry, and possibly two of them coincide in the most prominent and distinctly broader band at $14\,879 \text{ cm}^{-1}$. A detailed vibronic analysis will be presented elsewhere, together with complementary luminescence data.

(e) Exchange Interactions. Magnetic susceptibility data were collected in the temperature range 3.4–300 K and corrected for diamagnetism. The temperature-independent paramagnetism was taken as $60 \times 10^{-6} \text{ cm}^3/\text{mol}$. Figure 5 shows a $1/T$ plot, in which antiferromagnetic exchange coupling interaction is to be seen by characteristic deviations from the Curie-Weiss law. The temperature dependence of the magnetic susceptibility of a pair of exchanged-coupled $S = 3/2$ ions, assuming an isotropic Zeeman effect, has been given elsewhere¹⁷ and takes the form

$$\chi_{\mu} = [Ng^2\beta^2/kT] \times \frac{2 \exp(A/kT) + 10 \exp(B/kT) + 28 \exp(C/kT)}{1 + 3 \exp(A/kT) + 5 \exp(B/kT) + 7 \exp(C/kT)} \quad (5)$$

with the following abbreviations: $A = 2J - 6.5j$; $B = 6J - 13.5j$; $C = 12J - 9.0j$. The exchange integral J was evaluated by fitting this equation to the experimental susceptibility data with a version of the simplex routine given by Olsson.³³ The fitting procedure presents some difficulties due to paramagnetic impurities, which is not unexpected in view of the preparation conditions. This was taken into account by use of eq 6, counting the paramagnetic mole fraction x .

$$\chi_{\text{calcd}} = (1 - x)\chi_{\text{Cr-Cr}} + xNg^2\beta^2/4kT + N\alpha \quad (6)$$

If the restriction $j = 0$ is introduced, no significant influence is to be seen; hence, there is no justification for retaining the biquadratic term in the Hamiltonian in the present case ($|j| < 0.05 \text{ cm}^{-1}$). From the simple Hamiltonian (2) a value of $-0.4 \pm 0.05 \text{ cm}^{-1}$ is obtained for the ground-state exchange integral J in connexion with $x = 0.01 \pm 0.005$.

In the remainder of this section the factors determining the sign and magnitude of J are discussed. Since exchange coupling is known to be strongly influenced by the actual geometry of binuclear complexes,^{31,34} the various interaction mechanisms have to be considered. For the more general Hamiltonian³⁵

$$H_{\text{ex}} = -\sum_{ij} 2J_{ij}s_i^z s_j^z \quad (7)$$

J can be expressed as an average of nine orbital parameters, J_{ij} ,

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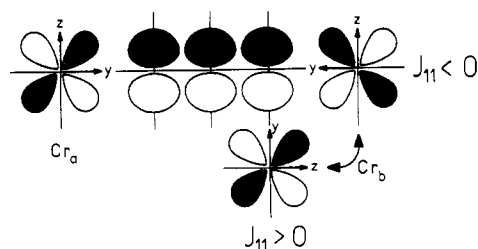


Figure 6. Antiferromagnetic and ferromagnetic coupling of $yz - yz'$ magnetic orbitals for 180 and 90° interactions.

where i and j refer to the singly occupied t_{2g} orbitals of chromium ions a and b , respectively:³⁵

$$J = \frac{1}{4} S_a S_b \sum_{ij} J_{ij} = \frac{1}{9} \sum_{ij} J_{ij} \quad (8)$$

Although no insight into the absolute magnitudes of the various J_{ij} values can be obtained from susceptibility data, each of the J_{ij} may represent ferro- or antiferromagnetic interaction, and J can be expressed by two opposing terms:

$$J = J^F + J^{AF} \quad (9)$$

Empirical rules for the prediction of the kind of magnetic exchange have been given by Goodenough³⁶ and Kanamori.³⁷ As mentioned above, there are three bridging modes possible for cyanate dimers. Considering first the hypothetical single-atom-bridged structures I and II, strong antiferromagnetic behavior would be expected through the exchange pathways $xy \parallel xy'$ (direct exchange) and $xz \parallel p_z \parallel xz'$ (superexchange), using the usual notations as given by Ginsberg.³⁸ By an examination of the present end-to-end structure (III), direct exchange can be neglected in view of the long Cr–Cr distance ($> 5 \text{ \AA}$). For a bis(μ -cyanato)nickel(II) dimer Hendrickson found Ni–N–C and Ni–O–C angles of 155.0 and 117.1°, respectively, which can be expected due to the possible hybridization structures of the cyanate ion.⁹ However, in this case significant deviations from a linear alignment are necessary to incorporate two bridging cyanate ions, contrary to the situation for a singly bridged cyanate compound. For single-atom bridging, two extreme geometries, a 90° bridging unit and a linear alignment (180°), are now discussed. At 90°, only one antiferromagnetic

pathway is active, $xy \parallel p_x \parallel xy'$, whereas 180° interaction additionally involves $yz \parallel p_z \parallel yz'$ (Figure 6). If the orbitals are numbered $yz \rightarrow 1$, $xz \rightarrow 2$, and $xy \rightarrow 3$, the antiferromagnetic contribution results from J_{33} in both cases, whereas J_{11} changes sign between the two bridging angles considered:

$$\begin{aligned} 90^\circ: J^{AF} &= J_{33} \\ 180^\circ: J^{AF} &= J_{11} + J_{33} \end{aligned}$$

According to the theory of Anderson,³⁹ kinetic exchange ($J < 0$) predominates over potential exchange ($J > 0$); hence, strong antiferromagnetic coupling is expected in the linear geometry by means of the π -overlap pathways through the cyanate bridge.

It is noted that experimental⁴⁰ and recent theoretical results⁴¹ have proved that even extended bridges can transmit important magnetic interactions between ions far from each other. On the other hand, 90° interactions would induce parallel spins in the low-energy state through ferromagnetic pathways.³⁸ Now with respect to the IR results, the qualitative interpretation of the magnetic data is straightforward when an end-to-end structure is assumed that shows only small deviations from linearity. Since antiferromagnetic contributions will decrease when the tetragonal symmetry of the bridging unit (180° case) is disturbed, net weak antiferromagnetism is observed. With respect to the nickel cyanate dimer,⁹ the bridging angles are significantly expanded in the complex under discussion, possibly caused by steric hindrance between ammonia groups ligated to different chromium ions of the dimer. This explanation of the magnetic behavior is supported by the results from the vibrational analysis. The bending mode $\delta(\text{N–C–O})$, which is degenerate only in tetragonal or higher symmetry, is not found to be split, indicating at most small deviations from linearity in the Cr–NCO–Cr bridging unit. However, a more precise study of exchange mechanisms requires detailed structural information.

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Registry No. $[(\text{NH}_3)_5\text{Cr}(\text{NCO})\text{Cr}(\text{NH}_3)_5]\text{Cl}_5$, 99617-61-5; D_2 , 7782-39-0; urea, 57-13-6.

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