Crystal structure and ligand field states of $[Cr(NH_3)_5NCO](NO_3)_2$*

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Abstract

The crystal structure of $[Cr(NH_3)_5NCO](NO_3)_2$ has been determined from three-dimensional X-ray diffractometer data. The compound crystallizes in the tetragonal space group $I4mm(C_{4v}{}^9)$, $Z=2$, lattice parameters $a=7.426(4)$ and $c=11.113(6)$ Å. The cation has $4mm(C_{4v})$ site symmetry consistent with a linearly coordinated cyanate group. The chromium ion deviates from the equatorial plane of ammine ligands by 0.06 Å toward the cyanato ligand, which was found to coordinate via its nitrogen atom. Structural information and optical spectra were combined in order to rationalize d–d transitions and to determine bonding properties of the NCO^- ligand. By using the parametrization of the angular overlap model (AOM), we obtained antibonding parameters $e_\sigma=6060$ cm^{-1} and $e_\pi=420$ cm^{-1}, respectively, from the fitting of quartet and doublet transitions. In the calculation of energies of the highly resolved doublet states, we evaluated the influence of the second coordination sphere ($NO_3{}^-$ anions). The large splitting of the first excited state, $^2E_g(O_h)$, was shown to originate predominantly from a low-symmetry contribution to the interelectronic repulsion, as earlier observed for related halogenopentaammine complexes.

Key words: Crystal structures; Electronic structure; Angular overlap model; Chromium complexes; Ammine complexes; Cyanato complexes

Introduction

The optical properties of pentaammine complexes of trivalent chromium have received much attention due to their interesting photochemical behaviour [1–3]. The elucidation of the underlying physical processes requires a profound knowledge of the energy level schemes which arise from the d^3 electron configuration. Although the ligand field approach has proved to be a powerful tool for rationalizing metal-localized electronic states in Werner-type transition-metal complexes, the exceptionally large splitting of the lowest excited state, $^2E_g(O_h)$, in many tetragonal Cr(III) complexes has been object of long-standing and controversial discussions [4–6]. In the case of halogenopentaammines, this splitting has been attributed to the interelectronic repulsion within the open d shell by introducing a low-symmetry parameter τ into the spherical (!) parametrization [7]. On the other hand, the influence of the second coordination sphere can also enlarge the ^2E_g splitting considerably [8].

Another point of interest concerns the potential ambidentate character of the cyanate ion [9]. While the thiocyanate group is well known in coordination compounds, structural data are very rare for cyanato complexes [10]. However, such information is often required to derive reliable band assignments from the optical spectra, because well resolved intraconfigurational d–d transitions are usually strongly influenced by the actual molecular geometry. Within the ligand field approach, the energy-level schemes of low-symmetry compounds are preferentially described within the framework of the angular overlap model (AOM), which explicitly accounts for the angular geometry of the chromophore [11–13]. Moreover, combining precise structural data with the observed transition energies should enable us to determine bonding properties of the NCO^- ligand in terms of the AOM parametrization, which uses local quantities to describe metal–ligand interactions of the σ and π type. Accordingly we attempted the growth of single crystals of $[Cr(NH_3)_5NCO](NO_3)_2$ and present here the first X-ray study and AOM analysis of a cyanato complex of Cr(III).

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*Dedicated to Professor Hans-Herbert Schmidtke on the occasion of his 65th birthday.

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Experimental

The nitrate salt of isocyanatopentaamminechromium(III) was prepared by thermal decomposition of $[Cr(urea)_6]^{3+}$ [14]. Crystals for the X-ray analysis were grown by slow evaporation of a saturated aqueous solution at room temperature, which was strictly kept in the dark to avoid photochemical reactions. Visible absorption spectra were measured with a Cary 4 spectrometer mounting microcrystalline powders with conductive grease on the cold head of a Cryovac helium cryostat.

X-ray reflections were recorded on a AED 2 (Siemens) diffractometer with variable ω/θ scan using Mo Kα radiation ($\lambda = 0.71073$ Å) [15]. The structure was solved by means of the Patterson function and refined as usual with the observed reflections only ($|F_o| > 4\sigma(F_o)$). The positions of the H atoms could not be accurately located in the residual electron density map, probably as a consequence of a more or less free rotation around the Cr–NH_3 axes. Some details of the X-ray analysis are presented in Table 1. All calculations were done with the SHELXTL PLUS program system [16] on a VAX station 3200 (DEC).

Results and discussion

Crystal structure

Drawings of the crystal structure are shown in Fig. 1; parameters for all non-hydrogen atoms are given in Table 2. $[Cr(NH_3)_5NCO](NO_3)_2$ crystallizes in the *anti*-$K_2[PtCl_6]$ type structure, distorted in the direction of the long NCO groups, which were found to be perfectly linear and unambiguously coordinated through the N atom. The cations form a pseudocubic close packing, all tetrahedral holes are occupied by the anions. The symmetry of the complex cations as well as the site

TABLE 1. Crystallographic data as well as experimental and computational conditions for the X-ray analysis

Crystal system	tetragonal
Space group; Z	$I4mm$; 2
a (Å)	7.426(4)
c (Å)	11.113(6)
V (Å^3)	612.8(3)
D_{calc} (mg mm^{-3})	1.64
μ(Mo Kα) (mm^{-1})	0.95
Crystal dimensions (mm)	0.2×0.2×0.3
$2\theta_{max}$ (°)	70
Unique reflections	425
Unique observed reflections ($|F_o| > 4\sigma(F)$)	390
Weighting scheme	$w = 1/(\sigma^2(F) + 0.0004F^2)$
Parameters refined	35
R; R_w (obs. data)	0.041; 0.051
$\Delta\rho$: min.; max. (e Å^{-3})	−0.32; 0.48

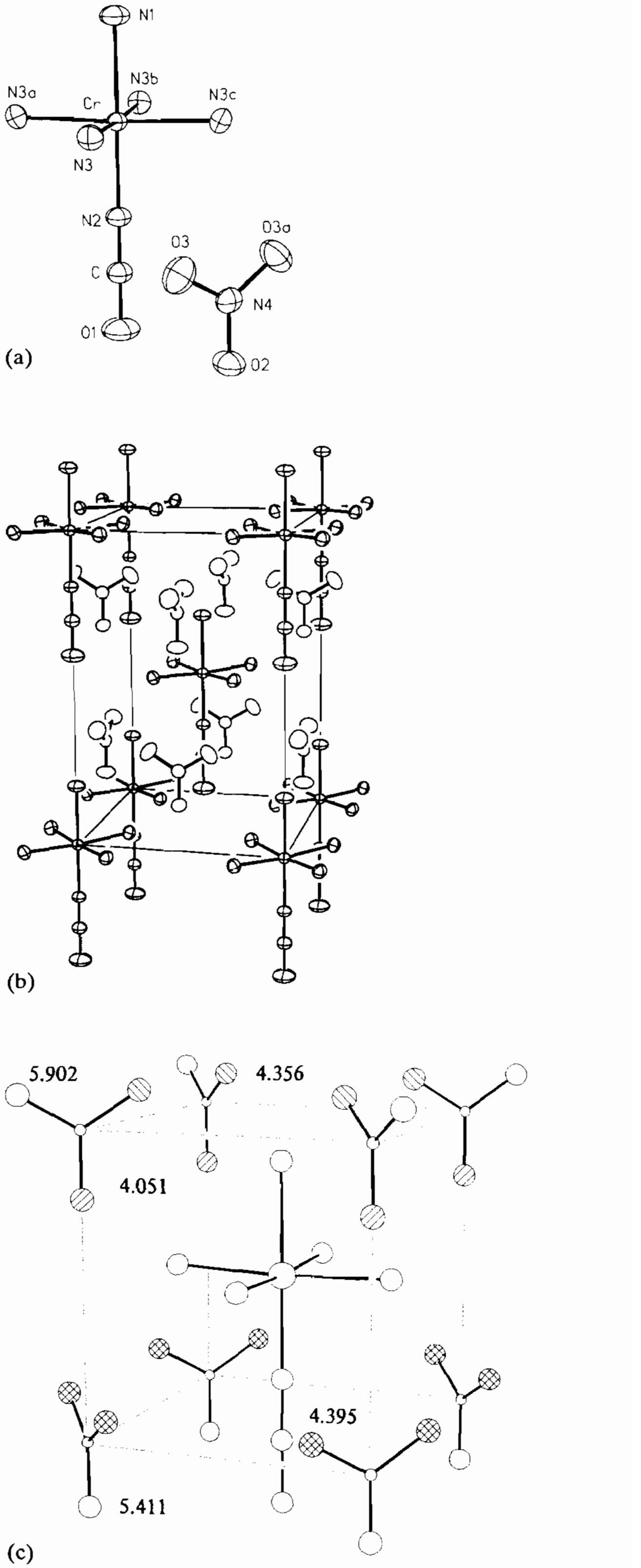

Fig. 1. $[Cr(NH_3)_5NCO](NO_3)_2$: (a) ions, (b) unit cell, (c) second coordination sphere of the Cr^{3+} ion, consisting of eight NO_3^- ions in a CaF_2 like arrangement. The distances Cr–$O_{(NO_3)}$ are given. The marked O atoms were included in some AOM calculations. Symmetry code: a: x, $-y$, z; b: $-x$, $-y$, z; c: x, y, z.

TABLE 2. Final atomic coordinates and U_{eq} (Å^2) with e.s.d.s in parentheses

Atom	Site	x	y	z	$100U_{eq}$^{a}
Cr	2a 4 mm	0	0	0	3.89(2)
O1	2a 4mm	0	0	0.3901(9)	11.8(4)
O2	4b 2mm	0.5	0	0.3542(5)	7.9(2)
O3	8d .m.	0.5	0.1438(6)	0.1886(4)	9.0(2)
N1	2a 4mm	0	0	−0.188(1)	6.9(3)
N2	2a 4mm	0	0	0.1768(8)	5.5(2)
N3	8c ..m	0.1979(3)	=x	−0.0056(4)	5.43(6)
N4	4b 2mm	0.5	0	0.2468(9)	5.2(2)
C	2a 4mm	0	0	0.2814(9)	5.9(2)

$^a U_{eq} = (1/3)(U_{11}a^2a^{*2} + U_{23}bcb^*c^* \cdot \cos\ \alpha \ldots)$.

TABLE 3. Bond lengths (Å) and angles (°)

Cr–N1	2.09(1)	N1–Cr–N2	180.0
Cr–N2	1.965(9)	N1–Cr–N3	88.3(1)
Cr–N3	2.079(3)	N2–Cr–N3	91.7(1)
N2–C	1.16(1)	N3–Cr–N3a	89.9(1)
C–O1	1.21(1)	N3–Cr–N3b	176.5(2)
N4–O2	1.19(1)	Cr–N2–C	180.0
N4–O3	1.248(7)	N2–C–O1	180.0
		O2–N4–O3	121.2(4)
		O3–N4–O3a	117.6(8)

symmetry for the Cr atom is C_{4v}, however, the angular geometry of the [CrN$_6$] chromophore is very close to that of a regular octahedron; the relevant bond lengths and angles are collected in Table 3.

The NCO$^-$ ligands are aligned parallel and point with their free ends to the unoccupied octahedral hole (Fig. 1(b)), the large displacement parameter of the atom O1 indicating a tendency toward disorder. There is no significant structural *trans*-effect for the axial ammine atom N1 (see Table 3). The Cr atom lies only 0.06 Å out of the equatorial plane of the ammine ligands and is displaced toward the cyanato group. The smallest donor–acceptor distance (N1 · · · O3: 2.98 Å; O3 in x-0.5, y-0.5, z-0.5) is quite common for hydrogen bonding. The participating H atom, like the others on N1, are at least fourfold disordered by reason of symmetry. The unequal contributions of the nitrate O atoms to possible hydrogen bonding at greater distances, O2 · · · N3 at 3.10 Å (4x) and O3 · · · N3 at 3.14 Å (2x), could explain the different bond lengths N4–O within the nitrate anion. The site symmetry of the latter in the crystal is reduced from $\bar{6}m2$ (D_{3h}) to $2mm$(C_{2v}). The second coordination sphere of the chromium ion, with 16 O atoms of only slightly different Cr–O distances, is illustrated in Fig. 1(c). The angle M–N–C for a monodentate NCO ligand varies from 128.1° (M = H) [17] through 139.3° (M = Ni) [18] and 160.9° (M = Co) [19] to 180° (this work). Bush and Sim reported the crystal structure of (π-C$_5$H$_5$)Cr(NO)$_2$NCO with a CrNCO geometry similar to the present one [20].

Ligand field transitions

The room temperature absorption spectrum of an aqueous solution shows two spin-allowed bands at 20 300 and 27 300 cm^{-1} [14] which are due to transitions $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4T_{1g}$ as typically observed for octahedrally coordinated Cr(III) complexes. As expected from the similar position for ammonia and N-bonded isocyanato ligands in the spectrochemical series, these bands are not split either in the solution spectrum or in the low-temperature spectrum of the microcrystalline powder, where the maxima are slightly shifted to 20 850 and 27 600 cm^{-1} (Fig. 2). For tetragonally coordinated d^3 ions, however, ligand field theory predicts the $^4B_2(^4T_{2g})$ level exactly at the energy of the parent $^4T_{2g}$ state, i.e. at 22 300 cm^{-1} (= 10Dq(NH$_3$)) as obtained from the helium temperature absorption spectrum of the related hexaammine complex [21]. Then the red shift (1450 cm^{-1}) of the maximum of the first quartet band from the octahedral hexaammine complex allows an estimate of the ligand field strength of the isocyanate ligand by use of the following relation for C_{4v} symmetry [22]:

$$Dq(\mathrm{NCO}) = Dq(\mathrm{NH_3}) - \frac{2}{5}\,1450\ \mathrm{cm^{-1}} = 1650\ \mathrm{cm^{-1}}$$

A Gaussian band deconvolution of the absorption pattern (least-squares fit) yielded maxima at 20 100, 21 800, and 26 800, 27 900 cm^{-1} for the tetragonally split levels of $^4T_{2g}$ and $^4T_{1g}$, respectively. These data are certainly rather approximate, and assignments to definite split levels cannot be obtained from this procedure alone;

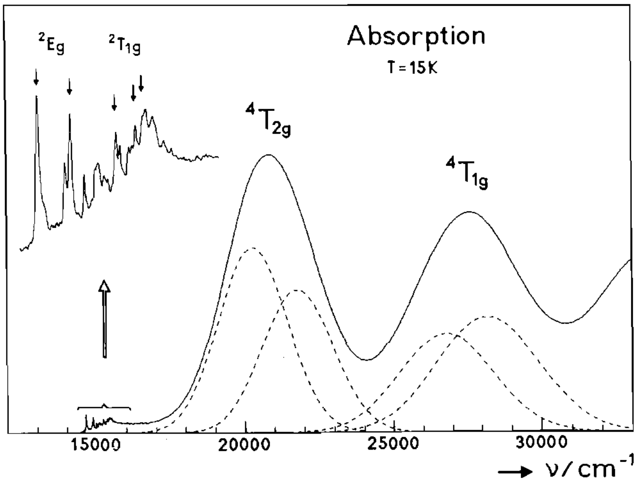

Fig. 2. Absorption spectrum of microcrystalline [Cr(NH$_3$)$_5$NCO](NO$_3$)$_2$ obtained at T = 15 K including a band deconvolution of quartet transitions by means of Gaussian band shapes. Arrows indicate electronic origins in the region of the lowest doublet transitions.

nevertheless, they can be helpful in deriving the AOM parameters of the isocyanato ligand (see next section).

In the intercombination band region of ${}^4A_{2g} \rightarrow {}^2E_g$, ${}^2T_{1g}$ transitions, on the other hand, a great deal of fine structure can be observed, which is illustrated in Fig. 2. These doublets are split by the tetragonal ligand field (C_{4v} symmetry) into ${}^2B_1$, ${}^2A_1$ (${}^2E_g$) and ${}^2E$, ${}^2A_2$ (${}^2T_{1g}$), or the Kramers' doublets $\{\Gamma_6, \Gamma_7\}$ and $\{\Gamma_6, \Gamma_7, \Gamma_6\}$, respectively, when spin–orbit coupling is taken into account. A careful examination of the absorption band shape measured at low temperature [6] has revealed that the two most prominent lines at 14 678 (Γ_6) and 14 891 (Γ_7) cm^{-1} are due to zero-phonon transitions from the ground state* into the low-symmetry split components of ${}^2E_g(O_h)$. The origins due to the higher ${}^2T_{1g}(O_h)$ were identified among a series of overlapping vibronic lines of comparable intensities at positions 15 256 (Γ_6), 15 378 (Γ_7) and 15 424 (Γ_6) cm^{-1}.

AOM calculations

In order to study the factors which influence the d level splittings we have performed a series of calculations by diagonalizing the full 120×120 secular determinant which arises from the perturbated d^3 system. Since the π interaction with the ammonia ligands can be reasonably neglected ($e_\pi = 0$), a total of at least six electronic parameters is involved in the calculations describing the interelectronic repulsion in terms of two Racah parameters B and C, the spin–orbit coupling by the quantity ζ, the the metal–ligand interactions by means of the three AOM parameters $e_{\sigma NH_3}$, $e_{\sigma NCO}$ and $e_{\pi NCO}$. Therefore, we are immediately confronted with the problem of overparametrization, which may allow for a good fit even with incorrect assignments or unphysical parameter sets. On the other hand, the (spherical) Racah parameters do not influence the low-symmetry level splittings considered here; they can be obtained in good approximation from the quartet band separation ($\approx 12B$) and from the position of the lowest doublet ($\approx 9B + 3C$) without further variation. Since AOM parameters have been found to be transferable between similar compounds [11–13], $e_{\sigma NH_3}$ is well established from calculations on other pentaammine complexes to have a value around 7300 cm^{-1} [6, 8]. Moreover, from the familiar relation valid for octahedral symmetry

$$10Dq = 3e_\sigma - 4e_\pi$$

a further reduction of the parameter space is derived when the cubic ligand field strength of the isocyanate ligand is considered (see above). Using these restrictions, no more than two parameters, i.e. the spin–orbit coupling constant** ζ and the ratio $e_{\sigma NCO}/e_{\pi NCO}$, are required to calculate d–d transition energies in $[Cr(NH_3)_5NCO](NO_3)_2$.

Since splittings of the broad quartet bands are not spectroscopically resolved for the present compound (and will be calculated to be relatively small) we focus the following discussion on the energy level sequence of the five lowest Kramers' doublets. Figure 3 illustrates the influence of spin–orbit coupling and the nature of the Cr–NCO bonding, respectively, on these states. Obviously, the experimental transition energies, in particular the ${}^2E_g$ splitting, cannot be reproduced for any choice of these quantities. This result is not changed, when all parameters involved are varied freely, in accordance with earlier calculations on halogenopentaammines [4, 6, 7].

However, two other factors may come into play here: contributions of the second coordination sphere to the ligand field potential acting on the Cr^{3+} ions, and/or the inadequate description of the interelectronic repulsion in low-symmetry complexes. In the first case, Hoggard and Lee have shown that perturbations of the d electrons caused by counterions enlarge the doublet splittings in $K_3[Cr(CN)_6]$ considerably [8]. Therefore, we have included in our calculations the second coordination sphere which consists of oxygen atoms from eight surrounding NO_3^- anions, the sixteen nearest oxygens lying at distances between 4.05 and 4.40 Å from the central Cr^{3+} ion (see Fig. 1(c)). Because the deviations in M–L distances of the first coordination sphere are usually small, e.g. in the present case less than 0.01 Å for axial and equatorial Cr–NH_3 distances (see Table 3), they can reasonably be neglected in the

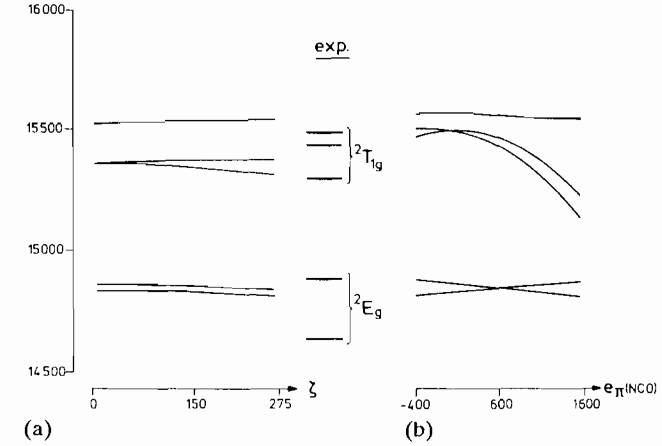

Fig. 3. Energy level diagrams for the lowest doublets in $[Cr(NH_3)_5NCO]^{2+}$. Parameter values: $B = 600$, $C = 3000$; $e_{\sigma NH_3} = 7300$, $e_{\pi NH_3} = 0$. (*a*) $e_{\sigma NCO} = 6833$, $e_{\pi NCO} = 1000$; (*b*) $\zeta = 200$, $e_{\sigma NCO} = (16500 + 4e_{\pi NCO})/3$; all in cm^{-1}.

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*The spin–orbit splitting of the ground state ${}^4B_1(C_{4v})$ is too small (< 1 cm^{-1}) to be observed in our optical spectra.

**$\zeta_{free\ ion} = 275$ cm^{-1}; $\zeta_{complex} < \zeta_{free\ ion}$.

AOM parametrization. Otherwise, the larger variations common for the distances from the central ion to the counterions must clearly be considered. Unfortunately, analytical forms for the dependencies of e_σ and e_π parameters on the metal–ligand distance R are *de facto* not known, in particular, for such a wide range of 1.90 to 4.40 Å. On the other hand, it is reasonable to assume π contributions to be negligibly small for such large distances. Figure 4(a) shows the influence of σ type interactions of the second coordination sphere on the relevant doublet energies. The different Cr–O distances between 4.05 and 4.40 Å were considered by means of an R^{-3} dependence that has already been successfully applied for Cr-doped oxide lattices [23]. These calculations show smaller doublet splittings when the second sphere comes into play, an effect just opposite to the experimental observations. This result is not changed when the variation of $e_{\sigma NO_3}$ with the metal–ligand distance is altered* using inverse powers of R between 3 and 5.

Another plausible extension concerns the incomplete treatment of the interelectronic repulsion in conventional ligand field calculations. To avoid the inflation of parameters that occurs even in cubic symmetry [24], matrix elements are used, which contain only two variables, the spherical parameters B and C. This shortcoming has been discussed by several authors, particularly by Jørgensen, who introduced nephelauxetic ratios β_{55}, β_{35},..., to describe the intra- and interconfigurational d–d transitions in optical spectra [25]. Recently, Schmidtke *et al.* have shown that weighting the repulsion integrals by the Stevens orbital-delocalization coefficients τ_i (<1) can significantly improve the theoretical treatment for the pentaammine complexes of Cr(III) [7]. Since we are concerned here with pure spin-flip transitions within the $(t_{2g})^3$ electron configuration, and because NH_3 ligands do not contribute to π bonding, only one additional parameter is required for the present C_{4v} symmetry: the reduction factor $\tau=\tau_{xz}=\tau_{yz}$ that considers a distinct π delocalization of d electrons toward the axial NCO^- ligand. Figure 4(b) illustrates this symmetry-adapted nephelauxetic effect on the lowest energy levels, showing the experimental splitting of 213 cm^{-1} well reproduced at τ values close to 0.99. This result agrees with the value of 0.989, which is obtained from the difference between two diagonal elements of the tetragonal perturbation matrix [7]

$$2\tau^2(\tau^2-1)=[(\Gamma_6(^2B_1)-\Gamma_7(^2A_1)]\,/\,[3B+C]$$

when adequate values for the Racah parameters involved are used.

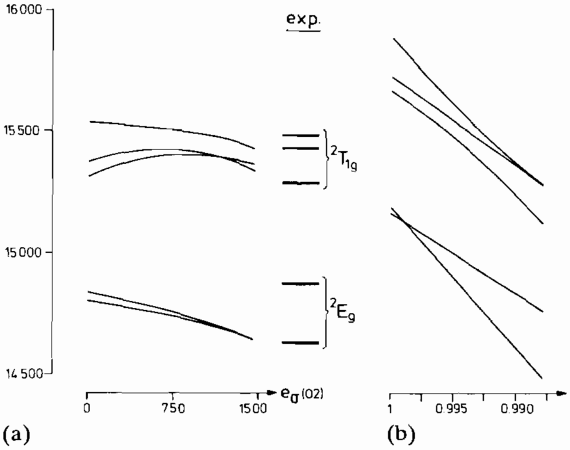

Fig. 4. Energy level diagrams for the lowest doublets in $[Cr(NH_3)_5NCO]^{2+}$ showing the dependence on LF contributions due to the second coordination sphere (a) and the axial π delocalization (b). Parameter values as given for Fig. 3(a) ($\zeta=200$ cm^{-1}).

TABLE 4. Observed and calculated d^3 energies in $[Cr(NH_3)_5NCO](NO_3)_2$. Parameters were partly obtained from an optimization procedure (see text): $e_{\sigma NH_3}=7200$, $e_{\pi NH_3}=0$, $e_{\sigma NCO}=6060$, $e_{\pi NCO}=420$, $B=645$, $C=3430$, $\tau=0.99$, $\zeta=230$; all data in cm^{-1}

	Assignment	Observed	Calculated
$^4T_{1g}$	^4E	27900[a]	27500
	$^4A_2$	26800[a]	27100
$^4T_{2g}$	$^4B_2$	21800[a]	21600
	^4E	20100[a]	20100
$^2T_{1g}$	Γ_6	15424	15350
	Γ_7	15378	15324
	Γ_6	15256	15183
^2E_g	Γ_7	14891	14891
	Γ_6	14678	14671
$^4A_{2g}$	Γ_6		0.13
	Γ_7	0	0

[a] Obtained from the Gaussian band deconvolution.

Finally, we tried to improve the calculated energy level scheme by using a fitting procedure which is based on the Powell algorithm [23]. We started with the optimization of the yet unknown AOM parameters for the σ and π type interactions with the isocyanato ligand, other parameters being assigned to reasonable values (see above). In a second step, all parameters involved were allowed to vary freely. By this procedure we readily obtained an excellent fit for the observed quartet and doublet energies. In particular, the calculated splittings of ^2E_g ($=220$ cm^{-1}) and $^2T_{1g}$ ($=167$ cm^{-1}) agree very well with the experimental data (213 and 168 cm^{-1}, respectively). Reasonable band maxima were also derived for the higher quartet transitions, although the individual spin–orbit components are not resolved here

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*The crystal field parameter Dq shows an R^{-5} dependence on the metal–ligand distance.

(see Table 4). The optimization routine yielded $e_{\sigma NCO}=6060\pm200$ cm^{-1}, $e_{\pi NCO}=420\pm150$ cm^{-1} and $\tau=0.990\pm0.001$; the other parameters are not significantly affected by the measured band splittings. It is noted that the final parameter values may depend somewhat on explicit weighting factors which were introduced in order to balance the spectral resolution for quartet and doublet transitions [8]. However, the unusually large ^2E_g splitting was clearly shown to originate from the distinct π interaction of the metal d electrons with the isocyanato ligand, which can be adequately described by a symmetric reduction of the relevant repulsion integrals in the d^3 perturbation matrix. Other possible effects, like the geometric deviation of the Cr^{3+} ion out of the plane defined by the equatorial ammonia ligands, or the influence of the nearest coordination sphere, as defined by oxygen atoms of the NO_3^- counterions, could not be substantiated from the fitting of the experimental energy level scheme.

The present application of the AOM leads to some conclusions concerning the bonding properties of the NCO^- ligand. The AOM antibonding parameters are significantly smaller when compared with the N-bonded thiocyanate ligand* or with π contributions of halide ligands [7]. This is reasonably explained by the strong electron-withdrawing property of the oxygen leading to a more important contribution of the resonance form (a) in isocyanato complexes. This effect enlarges the role of sp-hybridization at the nitrogen atom, explaining smaller values for $e_{\sigma NCO}$.

Such properties can also be illustrated within the MO theory: extended Hückel calculations on NCX^- ions show, for example, a larger expansion of HOMO and LUMO orbitals toward the metal ion for the N-bonded thiocyanate anion. Consequently, the metal–ligand overlap integrals, which contribute to the covalent part of the respective AOM parameters [26], can be expected to become significantly larger here.

Supplementary material

Crystallographic data have been deposited as Supplementary Publication No. CSD 400587. Copies can be obtained through the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen 2, Germany.

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*$e_{\sigma NCS}=6600$ cm^{-1}; $e_{\pi NCS}=950$ cm^{-1} [26].